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TECHNICAL REPORT
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**PHYSICAL AND RHEOLOGICAL PROPERTIES
OF
FLUORONITROSO RUBBERS
Final Report**

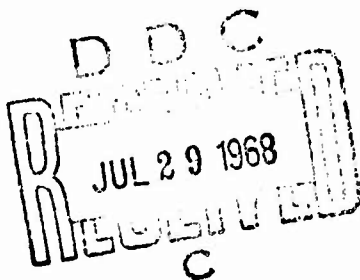
by

G. L. Ball III, I. O. Salyer,
J. V. Pustinger and H. S. Wilson

Monsanto Research Corporation
Dayton Laboratory, Dayton, Ohio

Contract No. DA19-129-AMC-151(N)

April 1967



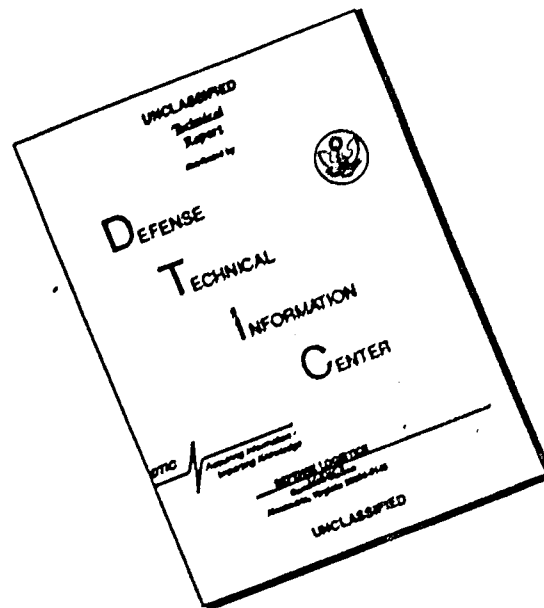
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RUBBERS

G. L. Ball, III, et al

Monsanto Research Corporation
Dayton, Ohio

April 1967

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G.L. Ball III, I.O. Salyer
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Monsanto Research Corporation
Dayton Laboratory
Dayton, Ohio 45407

Contract No. DA19-129-AMC-151(N)

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Clothing and Organic Materials Division
U. S. ARMY NATICK LABORATORIES
Natick, Massachusetts 01760

FOREWORD

One of the requirements of the U.S. Army is a rubber which has excellent solvent resistance as well as good flexibility at low temperatures. Research has shown that a nitroso rubber gum stock, a copolymer of tetrafluoroethylene and trifluoronitrosomethane, has this combination of properties to a high degree. Pound quantities of this gum stock have been prepared by the Thiokol Chemical Corporation. The physical and rheological studies of this gum stock were undertaken by the Monsanto Research Corporation with emphasis on molecular structure, solvent resistance, thermal stability, and some effects of curing conditions. Their results are contained in this report. In particular, their study of the molecular weight distribution, gel content, volatiles, and unexpected chemical groups, sheds new light on certain structural factors which should contribute to the synthesis of similar polymers with improved properties.

The work covered in this report was performed over a two-year period by G.L. Ball III, I.O. Salyer, H.S. Wilson, and J.V. Pustinger of the Monsanto Research Corporation, Dayton Laboratory, Dayton, Ohio, under Contract DA19-129-AMC-151(N).

The U.S. Army Natick Laboratories Project Officer was Dr. Robert A. Prosser, and the Alternate Project Officer was Dr. Nathaniel S. Schneider.

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TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	x
I. INTRODUCTION.....	1
II. SUMMARY.....	2
III. EXPERIMENTAL DATA.....	5
A. Solvents For The $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymer.....	5
B. Fingerprinting of The $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymer Batches.....	6
C. Solution Viscosities.....	7
D. Elemental Analysis.....	8
E. Infrared Analysis.....	8
F. Nuclear Magnetic Resonance Analysis.....	9
G. X-ray Analysis.....	9
H. Mass Spectrographic Analysis.....	9
I. Thermogravimetric Analysis.....	10
J. Differential Thermal Analysis.....	10
K. Solvent/Nonsolvent Systems For The $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymer.....	11
L. Fractionation Of The $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymer By The Elution Technique.....	11
M. Molecular Weight Determinations Of $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Fractions By Light-Scattering Analysis.....	12
N. Density Of The $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymer Gum.....	13
O. Qualitative and Quantitative Analysis Of Contaminants In Production Lots Of $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$	13
P. Linear Thermal Expansion Of The $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymer.....	13
Q. 1000 Cycles Per Second Modulus By Rebound Method Of The $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Gum.....	14
R. Amine Degradation Of The $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Gums.....	14
S. Formulations and Cure Conditions Of Amine- Cured $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymer.....	15
T. Physical Mechanical Properties Of The Amine- Cured $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Rubber.....	17
U. Solvent and Chemical Resistance Of The Amine- Cured $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Rubbers.....	18
V. Thermogravimetric Analysis Of The Amine- Cured $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymer.....	19

TABLE OF CONTENTS

	<u>Page</u>
IV. DISCUSSION.....	20
A. Solvents For The $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymer.....	20
B. Fingerprinting Of The $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymer Batches.....	21
C. Solution Viscosities.....	22
D. Elemental Analysis.....	23
E. Infrared Analysis.....	2
F. Nuclear Magnetic Resonance Analysis.....	25
G. X-ray Analysis.....	25
H. Mass Spectrographic Analysis.....	25
I. Thermogravimetric Analysis.....	27
J. Differential Thermal Analysis.....	28
K. Solvent/Nonsolvent Systems For The $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymers.....	28
L. Fractionation Of The $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymer By The Elution Technique.....	29
M. Molecular Weight Determinations and Distributions Of The $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymers....	31
N. Density Of $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymer Gum.....	34
O. Qualitative and Quantitative Analysis Of Contaminants In Production Lots Of $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$..	34
P. Linear Expansion Of The $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymer..	35
Q. Glass Transition Of The $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymer Gum At 1000 Cycles Per Second By Rebound Method.....	36
R. Amine Degradation Of The $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Gums.....	36
S. Formulation, Cure Conditions, and Mechanical Properties Of Amine-Cured $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymers	37
T. Solvent and Chemical Resistance Of The Amine- Cured $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Rubbers.....	42
U. Thermogravimetric Analysis Of The Amine- Cured $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymer.....	43
V. CONCLUSIONS.....	44
VI. REFERENCES.....	50
APPENDICES	
A. Tables.....	51
B. Figures.....	68
C. Solution Cleaning and Viscosity Techniques....	116
D. Fractionation Procedures.....	120
E. Light-Scattering Procedure.....	123
F. Details of Formulation, Curing, and Physical Testing Of The $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Rubber.....	125
G. Steel Preparation Procedure.....	130
H. NMR And IR OF $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Solvents.....	131

LIST OF TABLES

	<u>Page</u>
1. Elemental Analysis and "Atypicality" of $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Gums	52
2. Solubilities of $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ In FC-75 and Benzotrifluoride	53
3. Elution Fractionation of $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Gum XP5702 Following Selective Deposition - Run No. 3	54
4. Elution Fractionation of $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Gum XP5702 Following Selective Deposition - Run No. 4	55
5. Elution Fractionation of PCR-Bulk Polymerized $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymer Following Selective Deposition	56
6. "Apparent" Linear Thermal Expansion Coefficients of $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Gums	57
7. Molecular Weight Degradation of $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ By Amines	58
8. Compounding Recipes and Mechanical Test Results of Amine-Cured $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Rubbers	59
9. $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Rubber Hardness Values Prior To and After Curing in The Ball Rebound Apparatus	63
10. Solvent and Chemical Resistance of An Amine-Cured $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Rubber #37566 - Cure #1	64
11. Swell of $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Rubbers in FC-75	65
12. NMR Spectrographic Data and Assignments For $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Gums	66
13. Mass Spectrographic Mass Assignments For The $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymer	67

LIST OF FIGURES

	<u>Page</u>
1. Reduced and Inherent Viscosities of XP5702, XP5675, and 3M-56703 $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymers In FC-75 and FC-43 Fluorocarbon Solvents at 25°C	69
2. Reduced and Inherent Viscosities of XP5702 and XP5675 $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymers in Freon 113 at 35°C	70
3. Vicat Softening Temperatures for XP5675 and XP5702 $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymers As Received	71
4. Vicat Softening Temperatures of XP5812 and XP5704 $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymers As Received	72
5. Vicat Softening Temperatures of 0.5 Molar Ratio $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Terpolymer, PCR-Solution, and PCR-Bulk $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymers	73
6. Vicat Softening Temperature For Vacuum Dried XP5675 and XP5702 $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymers	74
7. Reduced and Inherent Viscosities of The XP5702 $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymer in FC-75 and FC-43 Fluorocarbon Solvents at 25°C	75
8. Reduced Viscosities of The PCR-Bulk and PCR-Solution $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymers in FC-75 Fluorocarbon Solvent at 25°C	76
9. Infrared Spectrum of The $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Gum Sample XP5675	77
10. Infrared Spectrum of The $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Gum Sample XP5702	77
11. Nuclear Magnetic (F^{19}) Resonance Spectrum of The $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Gum Sample XP5675	78
12. Actual Mass Spectra From Mass 15 to 50 For XP5675 $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Gum (100°C)	79

LIST OF FIGURES (CONTINUED)

	<u>Page</u>
13. Mass Spectrograph Pressure During Isothermal Runs On Samples XP5675, Vacuum-Dried XP5675, 3M-56703-3, and XP5812	80
14. Most Prominent Ionic Species From 50 Up To 275°C of Sample XP5675	81
15. Most Prominent Ionic Species From 50 Up To 275°C of Sample XP5675	82
16. Most Prominent Ionic Species From 50 Up To 275°C of Sample of Vacuum-Dried XP5675	83
17. Most Prominent Ionic Species From 50 Up To 275°C of Sample of Vacuum-Dried XP5675	84
18. Most Prominent Ionic Species From 50 Up To 250°C of Sample 3M-56703-3	85
19. Most Prominent Ionic Species From 50 Up To 250°C of Sample 3M-56703-3	86
20. Thermogravimetric Analysis Curves For CF ₃ NO/C ₂ F ₄ Copolymer Sample XP5675 Before and After Vacuum Drying 16 Hours at 80°C	87
21. Thermogravimetric Analysis Curve for CF ₃ NO/C ₂ F ₄ Copolymer Sample 3M-56703-3	88
22. Composite of Total and Differential Weight Loss of CF ₃ NO/C ₂ F ₄ Copolymer Sample XP5675 in Helium and Air	89
23. Differential Thermographs of Three CF ₃ NO/C ₂ F ₄ Copolymers (Low Temperature)	90
24. Total and Differential Weights As A Function of Viscosity For The CF ₃ NO/C ₂ F ₄ Copolymer XP5702 Elution Fractionation #3 and #4	91

LIST OF FIGURES (CONTINUED)

	<u>Page</u>
25. Total and Differential Weights As A Function of Viscosity For The Peninsular ChemResearch Bulk-Polymerized $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymer	92
26. Zimm Plot of $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymer Sample 3M-56703	93
27. Hc/τ $P(90^\circ)$ Versus Concentration For The $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymer Sample 3M-56703	94
28. Zimm Plot of $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymer Fraction No. 4, Run No. 2, Thiokol Sample XP5702	95
29. Hc/τ $P(90^\circ)$ Versus Concentration For The $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymer Fraction No. 4, Run No. 2, Thiokol Sample XP5702	96
30. Zimm Plot of $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymer Fractions No. 13 and 14, Run No. 3, Thiokol Sample XP5702	97
31. Hc/τ $P(90^\circ)$ Versus Concentration For The $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymer, Fractions No. 13 and 14, Run No. 3, Thiokol Sample XP5702	98
32. Zimm Plot of $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymer, Fraction No. 15, Run No. 3, Thiokol Sample XP5702	99
33. Hc/τ $P(90^\circ)$ Versus Concentration For the $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymer, Fraction No. 15, Run No. 3, Thiokol Sample XP5702	100
34. Infrared Spectra of White Precipitate From Thiokol $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Gum Sample XP5702	101
35. Infrared Spectra of Volatile Product From Thiokol $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Gum Sample XP5702	102
36. Nuclear Magnetic (F^{19}) Resonance Spectrum of Volatile From Thiokol $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Gum Sample XP5702	103

LIST OF FIGURES (CONTINUED)

	<u>Page</u>
37. Thermal Expansion of $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Gum Sample XP5702	104
38. Rebound Tester For 1000 Cycles Per Second Modulus	105
39. 1000 Cycles Per Second Modulus By Rebound Technique On $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Sample XP5675	106
40. Amine-Curing Cycles Of $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Gums Utilizing The 1000 Cycles-Per-Second Rebound Technique	107
41. Amine-Curing Cycles Of $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Gums Utilizing The 1000 Cycles-Per-Second Rebound Technique	108
42. Amine-Curing Cycles Of $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Gums Utilizing The 1000 Cycles-Per-Second Rebound Technique	109
43. 1000 Cycles Per Second Modulus By Rebound Technique On $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Rubber Samples 37559-4 and 37559-5	110
44. Modified Nonius Torsion Pendulum Apparatus For Determination of 3 cps Modulus	111
45. 3 cps Modulus By Modified Nonius Torsion Pendulum Technique Of $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Rubber Samples 37559-5 and 37559-8	112
46. Clash-Berg Torsion Modulus Of $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Rubber Sample 37559-5	113
47. Thermogravimetric Analysis In Air and Helium Of An Amine-Cured $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymer	114
48. Viscosity - Molecular Weight Relationship Of $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ In FC-75 (Isomers of Perfluorocyclic Ethers) at 25°C	115

ABSTRACT

Characterization of the copolymer trifluoronitroso-methane/tetrafluoroethylene was completed. The gum stock was primarily produced by the Thiokol Chemical Corporation and was supplied by the U.S. Army Natick Laboratories. No sample was submitted as representative of a production batch of the copolymer. The $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ copolymer was shown to be a low temperature gum with high solvent and chemical resistance and with a reasonable thermal stability up to 250°C . As received, the $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ gum was not readily cross-linked into a high-strength rubber. The gum samples consisted of 25-50% insoluble gel and ~3% insoluble basic magnesium carbonate trihydrate. The structure was shown to be: $[\text{N}-\text{CF}_2-\text{CF}_2-\text{O}]_x$. Violent decomposition of both the $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$

CF_3
gum and rubber occurred at $\sim 260^\circ\text{C}$. The initial decomposition was confirmed to be: $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4 \rightarrow \text{COF}_2 + \text{CF}_3\text{N} = \text{CF}_2$. The glass transition temperature of the gums covered a range of -41° to -49°C and that of the rubber was $\sim -49^\circ\text{C}$. The typical gum exhibited a bimodal molecular weight distribution with a lower portion at $\sim 2 \times 10^5$ and a higher portion at $\sim 6 \times 10^6$. A typical average M_W , M_N , and M_W/M_N was:

$M_W = 3.4 \times 10^6$, $M_N = 2.7 \times 10^4$, and $M_W/M_N = 125$. The Mark-

Houwink equation for $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ in FC-75 at 25°C is:

$[\eta] = 3.2 \times 10^{-5} \bar{M}_W^{0.72}$. Optimized cure conditions showed that lower cure temperatures and longer cure times were advisable, that MgO was valuable as a scavenger filler, and that a PCR-bulk-polymerized gum provided a significantly better rubber. The best mechanical properties obtained were 387 psi tensile strength and 527% elongation. Impurities and extremely high molecular weights were detrimental to providing good mechanical properties.

I. INTRODUCTION

This report consists of the results of the characterization of the copolymer trifluoronitrosomethane/tetrafluoroethylene. The gum stock was primarily produced by the Thiokol Chemical Corporation and was supplied to Monsanto Research Corporation by the U. S. Army Natick Laboratories. Two small samples were produced by Peninsular ChemResearch late in the program.

The length of the program was three years; however, samples were not received for the first year, thus limiting the actual characterization program to a two-year period.

No sample was submitted as a representative of a production batch of the copolymer gum. Therefore, the characterization was performed upon those samples that were received first, along with those most closely approximating the theoretical elemental analysis for $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$. No cured samples were received.

The Thiokol gum samples received were identified as ZR-561-XP5675, XP5702, XP5812, XP5887, XP5807, XP5704, 0.2 $\text{C}_2\text{F}_3\text{H}$ terpolymer, and 0.5 $\text{C}_2\text{F}_3\text{H}$ terpolymer. A 3M Company-produced sample and a bulk and solution-polymerized sample from Peninsular ChemResearch were also obtained.

While a complete and detailed characterization of the $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ copolymer was in order, the degree of worth of the copolymer in terms of solvent resistance, thermal stability, and low temperature flexibility was of prime interest.

The report is written in three primary sections consisting of Experimental Data, Discussion, and Conclusions. The experimental data are separated from the other two sections so that unbiased results can be interpreted as the reader pleases. Details of sample preparation, test techniques, and useful characterization data not pertinent to the discussion are presented in the Appendices.

II. SUMMARY

The characteristics, as well as the characterization techniques, of $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ gums were determined.

Techniques determined included:

1. The determination of the best solvent for solution studies and the application of the solvent to solution viscosity. The best solvent was 3M Fluorocarbon FC-75 (isomers of perfluorocyclic ether).

2. A fingerprinting procedure consisting of solution viscosity and Vicat indentation measurements to determine similarities between batches.

3. An elution fractionation procedure employing a solvent/nonsolvent system of isomers of perfluorocyclic ethers (FC-75) and benzotrifluoride by which ~1.5 grams of gum could be fractionated to 25 fractions.

4. Molecular weight analysis by light-scattering of the $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ gum in FC-75. Hc/τ $P(90^\circ)$ extrapolations to zero concentration provided molecular weights.

5. Dynamic glass transition temperature measurements utilizing the ball rebound method performed on whole gums, including the insoluble gel.

6. Cure-time temperature studies utilizing the ball rebound method.

Characterization included:

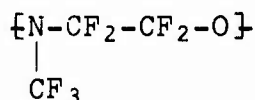
1. The Huggins K' and K'' constants for $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ in FC-75 at 25°C of 0.396 and 0.124, respectively.

2. Quantitative and qualitative analysis that showed the submitted gum samples consisted of 25 to 50% insoluble gel and ~3% insoluble basic magnesium carbonate trihydrate.

3. Elemental analysis confirming the $\text{C}_3\text{F}_7\text{NO}$ elemental nature to within 0.15%.

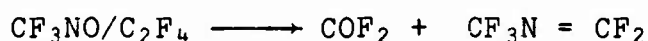
4. Infrared analysis exhibiting the C-F and C-O-N stretching and -CF₂-CF₂- bends.

5. Nuclear Magnetic resonance analysis defining the structure to be:



6. X-ray analysis indicating that the gum was non-crystalline from -70 up to 28°C.

7. Thermogravimetric analysis showing violent decomposition of both the CF₃NO/C₂F₄ gum and rubber at ~260°C. Weight losses starting at ~75°C were associated with lower boiling, lower molecular weight species. The decomposition was identical in air and an inert gas having been confirmed (with the aid of mass spectrographic analysis) to be:



8. Displacement density measurements showing densities of 1.937 ± 0.001 g/cc for the CF₃NO/C₂F₄ gum.

9. Molecular weight and molecular weight distribution that indicated a bimodal distribution of the typical gum with a lower portion at ~2 x 10⁵ and a higher portion ~6 x 10⁶. The low-molecular-weight portion represented an amount of 20% of the weight of the gum. The average M_W, M_N, and M_W/M_N for the gums were:

	<u>M_W</u>	<u>M_N</u>	<u>M_W/M_N</u>
XP5702 - R3	3.4 x 10 ⁶	2.7 x 10 ⁴	125
XP5702 - R4	3.4 x 10 ⁶	1.9 x 10 ⁵	18
PCR-bulk poly.	2.0 x 10 ⁶	2.3 x 10 ⁴	88

The M_N was weighted considerably by the low-molecular-weight portion.

10. Molecular weight-viscosity correlations that determined the Mark-Houwink equation for CF₃NO/C₂F₄ in FC-75 at 25°C to be:

$$[\eta] = 3.2 \times 10^{-5} \bar{M}_W^{0.72}$$

The a constant (0.72) demonstrated the improved solubility of the $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ gum in FC-75 over that in perfluorotributylamine (0.66) and Freon 113 (0.51).

11. Determination of the glass transition temperature of the gums by various techniques indicating a range of -41° to -49°C and that of the rubber to be $\sim -49^\circ\text{C}$. Reasonable flexibility of the rubber was indicated at temperatures as low as -55°C with probable utilization available to -70°C .

12. Determination of the highly degradative effects of amines upon the $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ gum with resulting significant losses in molecular weight.

13. Determination of optimum cure conditions on the various gums showing that lower cure temperatures and longer cure times were advisable, that MgO was valuable as a scavenger filler, and that the PCR-bulk-polymerized gum provided a significantly better rubber. The best mechanical properties obtained were 387 psi tensile strength and 527% elongation. Impurities and extremely high molecular weights were detrimental to providing good mechanical properties.

14. Determination of solvent and chemical resistance that indicated, but did not prove, high stability. The particular rubbers examined were poorly cross-linked; therefore, only lack of solubility and not lack of swelling was demonstrated.

The $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ copolymer was shown to be a low temperature gum with probable high solvent and chemical resistance and with reasonable thermal stability to 250°C . As received, the $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ gum was not readily cross-linked into a high strength rubber.

III. EXPERIMENTAL DATA

A. SOLVENTS FOR THE CF₃NO/C₂F₄ COPOLYMER

The CF₃NO/C₂F₄ copolymer was reported to exhibit characteristically a high degree of solvent resistance. This very nature, unfortunately, is not consistent with providing good solution studies. Highly fluorinated solvents had been reported to be the best for this gum (Ref. 1). Accordingly, the following solvents were evaluated for their usefulness in terms of time to solution and solution viscosity.

	<u>T_m, °C</u>	<u>T_{bp}, °C</u>
Perfluorotributylamine, (C ₄ F ₉) ₃ N [3M Brand Fluorochemical FC-43]	>23	175
Perfluorocyclic ether, isomers of, C ₈ F ₁₆ O [3M Brand Fluorochemical FC-75]	>23	100
Tetrachlorodifluoroethane, CCl ₂ FCCL ₂ F [Freon 112]	25	92
Trichlorotrifluoroethane, CCl ₂ FCClF ₂ [Freon 113]	>23	46

These solvents will be designated as FC-43, FC-75, Freon 112, and Freon 113 in further discussion.

As shown above, the Freon 112 melts at 25°C; therefore, at a room temperature of 23°C, solution with the nitroso gum could not be maintained. After a few unsuccessful attempts to provide solution up to 80°C with the Freon 112, the solvent received no further attention.

The XP5675 and XP5702 gums were put into solution in three remaining solvents. A period of at least 24 hours at 80°C was necessary to get the gum into solution in the FC-75 or in the FC-43. Because of the low boiling point of the Freon 113, an attempt was made to dissolve the gums in this solvent at 23°C. Solution did not occur in seven days. It was found, however, that when the temperature was raised to just 25°C, the gum dissolved as fast as it did in the FC-75 and FC-43 solvents.

Upon dissolving either the XP5675 or the XP5702 in any of the three solvents, a cloudy solution resulted. Filtering through extremely retentive, hardened filter paper removed only a minute portion of the cloudiness. Centrifuging for six hours (for the FC-75) and 12 hours (for the FC-43), followed by refiltering, was necessary to remove the cloudiness.

Although exact quantitative analyses of insoluble products in the gums were not conducted, due to the visible nonhomogeneity of the gum samples, the following typical percent insolubles were calculated from the initial and final concentrations of the solution:

<u>Solvent</u>	<u>% Insoluble or Lost ($\pm 8\%$)</u>	
	<u>XP5702</u>	<u>XP5675</u>
FC-43	29	14
FC-75	45	22

These insolubles were collected as a white substance (see Section O) and as a finely divided gel. No attempt was made to provide solution with previously reported poor organic solvents (Ref. 2).

B. FINGERPRINTING OF THE $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ COPOLYMER BATCHES

The fingerprinting of the $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ batches was an attempt to determine the similarity between production lots on a simplified basis. In essence, a quality control procedure was to be established.

Two techniques were explored--one utilizing solution viscosity and the other, the Vicat softening curve.

The solution viscosity fingerprinting technique consisted of measuring the solution viscosities of a gum in at least two different solvents. Typical results are shown in Figures 1 and 2, where three submitted gums were evaluated in three different solvents. Note the easily distinguishable differences and the fact that the intrinsic viscosity measurement was a resulting benefit.

The Vicat fingerprinting technique consisted of determining the indentation of a specified cross section as a function of temperature according to ASTM D1525-58T. The technique could be conducted upon an unmodified chunk of the gum sample and was normally performed from -75°C to above the softening temperature.

Typical Vicat curves are shown in Figures 3 through 5 for samples XP5675, XP5702, XP5812, XP5704, PCR-bulk and PCR-solution-polymerized copolymer and the 0.5 molar ratio terpolymer. Shown in Figure 6 are samples XP5675 and XP5702 which were treated by heating at 50°C for 16 hours in a vacuum of 3 mm Hg.

Fingerprinting by means of measuring solution viscosities in first one solvent followed by dilution with another solvent was found to be of little value. This was primarily because as much time and effort was expended as for measuring solution viscosities in two different solvents without the applicable intrinsic viscosity data resulting.

C. SOLUTION VISCOSITIES

The presence of substantial insoluble and volatile portions complicated the measurement of solution viscosities in the submitted gums. The cleaning procedure required prior to any viscosity measurement is outlined in Appendix C. This, of course, means that the evaluated specimens were not always entirely representative of the submitted sample.

Specimens that were not cleaned were tested and reported in quarterly reports early in the program (Ref. 3). The reproducibility of viscosity data was such as to prove it rather doubtful - although still representative.

A typical plot of reduced and inherent viscosities of the cleaned sample XP5702 in solvents FC-75 and FC-43 is shown in Figure 7 with the K' and K'' Huggins constants.

Figures 1 and 2 represent three different partially cleaned gums in the solvents FC-75, FC-43, and Freon 113.

Other viscosity data determined in a similar manner, utilizing the K' and K" constants to extrapolate the intrinsic viscosity, are found in various tables through this report.

The solution viscosities of the PCR-bulk and solution-polymerized copolymer samples are shown in Figure 8.

D. ELEMENTAL ANALYSIS

Carbon, hydrogen, nitrogen, fluorine, and oxygen (by difference) elemental analysis was performed on what visually seemed to be the more typical samples received from Thiokol along with two samples from Peninsular Chem-Research. These were samples XP5675, XP5702, XP5812, XP5887, PCR-bulk and PCR-solution.

The elemental analysis was performed in December of 1964 and repeated again in June of 1966. One sample, XP5675, was analyzed also in March of 1965 with sample XP5702 being analyzed after vacuum-drying at the same time.

The analyses are recorded in Table 1. The oxygen was determined by difference since it could not be measured directly in the presence of fluorine. Also included in Table 1 is an "Atypicality" term, which is a measure of the percent deviation of the analysis from theoretical. It is calculated from:

$$A = \left(\frac{\sum (X - \bar{X})^2}{N-1} \right)^{1/2}$$

where X = analysis value, \bar{X} = theoretical value, and N = the number of elements reported. The theoretical analysis for C_3F_7NO is shown for comparison.

E. INFRARED ANALYSIS

Typical infrared spectra for the copolymer CF_3NO/C_2F_4 are shown in Figures 9 and 10 for the samples XP5675 and XP5702. These samples were evaluated as received in the form of gum smears. Solvent IR spectra are shown in Appendix H.

F. NUCLEAR MAGNETIC RESONANCE ANALYSIS

The typical F^{19} resonance spectrum of the CF_3NO/C_2F_4 copolymer is shown in Figure 11. The test was performed at 40.0 Mc with a trifluoroacetic acid reference. The area ratios and reference positions are also shown in the figure.

Also see Section O. and Figure 36. Solvent NMR spectra are shown in Appendix H.

G. X-RAY ANALYSIS

X-ray analysis was performed from $-70^\circ C$ up to $23^\circ C$ with resultant diffuse diffraction patterns.

H. MASS SPECTROGRAPHIC ANALYSIS

A typical mass spectra of the copolymer CF_3NO/C_2F_4 (Sample XP5675) is shown in Figure 12. The figure covers the spectrum from mass 15 to mass 50 and, in this particular case, was observed at $100^\circ C$.

The mass spectra were observed in four different samples representing the 3M gum (56703-3), Thiokol samples XP5675, XP5812, and XP5675, that was precipitated from solution. This observation was conducted at various stabilized sample temperatures from 50 up to $275^\circ C$.

The observed mass spectrograph pressure as a function of temperature for these four samples is shown in Figure 13.

The most prominent ionic species observed by the mass spectrograph as a function of sample temperature is shown in Figures 14 through 19 for the Thiokol samples XP5675, the precipitated sample of XP5675, and the 3M sample 56703-3.

I. THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric analysis was performed on Thiokol samples XP5702 and XP5675, a vacuum-dried sample of XP5675, and the 3M gum 56703-3. The XP5675 sample was vacuum-dried for 16 hours at 80°C.

The thermogravimetric analysis curves for the sample XP5675 before and after drying are shown in Figure 20. The TGA was conducted in an 0.2 mm Hg vacuum at ~3°C per minute temperature heating rate. This is also a typical curve for sample XP5702.

The TGA of 3M sample 56703-3 is represented in Figure 21 under identical test conditions.

Isothermal TGA's in both helium and air were conducted on sample XP5675 at about 25°C intervals from 23°C up to 330°C. A composite of the integral and differential weight loss of the sample as a function of temperature is shown in Figure 22. Also shown is the TGA of a vacuum-dried sample of XP5675 heated in helium.

J. DIFFERENTIAL THERMAL ANALYSIS

Differential thermal analysis was performed on various $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ samples from -100°C up to 300°C. DTA's for samples XP5702, XP5675, and 3M 56703-3 (9690), representative of all samples tested, are shown in Figure 23 from -100°C to 100°C. The analysis was performed in glass sample wells with chromel alumel thermocouples, an air atmosphere, and a heating rate of 11°C per minute on ~40 mg sample.

The DTA curves from 100°C to 300°C are not shown. They consist of a straight-line portion up to ~250°C and then a sudden endothermic thrust which is caused by the explosive removal of the thermocouple from the sample well.

K. SOLVENT/NONSOLVENT SYSTEMS FOR THE $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ COPOLYMER

Our preference for FC-75 [isomers of $\text{C}_8\text{F}_{16}\text{O}$] as a solvent has previously been noted (see Section A). This solvent has a boiling point of $\sim 100^\circ\text{C}$ and is relatively non-viscous (0.65 cs) from room temperature to its boiling point. Various nonsolvents miscible in the FC-75 were tried. However, very few solvents were miscible in the FC-75. The benzotrifluoride was miscible and has a boiling point of $\sim 100^\circ\text{C}$ and about equal viscosity to the FC-75

The precipitation point at 23°C and a range of useful concentrations and temperatures for fractionation by column elution have been determined for sample XP5702, a higher molecular weight gum portion. The concentrations and temperatures are shown in Table 2.

L. FRACTIONATION OF THE $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ COPOLYMER BY THE ELUTION TECHNIQUE

Two samples of the XP5702 and the Peninsular Chemical Research bulk-polymerized $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ copolymer were fractionated in detail by the elution technique (Ref. 4).

The samples were cleaned by being put into solution in FC-75 solvent (isomers of perfluorocyclic ether), heating to 80°C , cooling, filtering, centrifuging, decanting the clear solution, evaporating the solvent, and recovering the soluble gum. A large portion ($\sim 25\%$) of insoluble gel was noted as removed from the gums during this cleaning.

The polymer samples were again put into solution in FC-75 (1 g in 29 ml at 85°C). A solvent/nonsolvent system was then prepared based on prior determinations (see Section K) of solvent/nonsolvent ratios. The systems consisted of a ratio of ~ 3 g polymer/100 ml FC-75/73 ml benzotrifluoride. Under these conditions, the polymers were all in solution at 70°C and precipitated at 25°C .

The elution column consisted of cleaned, pure silica sand of mesh particle size ranging from -40 to +200. N_2 gas was used as a back pressure to regulate the flow of the solvent over the sand. This column is described in Reference 4.

The column was maintained at 78°C by refluxing ethanol in the jacket and the polymer solution was heated to 80°C prior to pouring it on the column. The actual solution added consisted of ~1 g of sample (purified), 33 ml of FC-75, and 24 ml benzotrifluoride. After the solution was added, the column was cooled slowly in order to cause selective deposition of the polymer. A final drying using N₂ gas was provided.

Removal of the polymer fractions was accomplished by elution with solvent/nonsolvent mixtures of FC-75 and benzotrifluoride. The column was first flushed with 250 ml of benzotrifluoride in order to remove any impurities and to set the polymer to the substrate. Progressive elutions were then performed by solvent/nonsolvent mixtures.

The details and techniques of the various fractionations are spelled out in Appendix D. The more detailed fractionations were performed by elution at 56.5°C (boiling acetone), utilizing 1% solvent/nonsolvent increments progressively from 35% up to 55% solvent/nonsolvent ratios. The fractionations performed are shown in Tables 3, 4, and 5.

Following fractionation, the fractions were evaporated, weighed, and when sufficient sample was available, specific viscosities were determined in an 0.1% solution of FC-75.

Data were also accumulated on the FC-43 solvent and at 35°C.

The three fractionations are shown in Figures 24 and 25 as viscosity versus total and differential weight.

M. MOLECULAR WEIGHT DETERMINATIONS OF CF₃NO/C₂F₄ FRACTIONS BY LIGHT-SCATTERING ANALYSIS

The techniques required in cleaning the submitted CF₃NO/C₂F₄ copolymer, in preparing light-scattering solutions, and in performing the light-scattering measurements are detailed in Appendices C and E.

The light scattering determinations were performed in FC-75 at 25°C for a number of sample solutions represented by the Zimm and Hc/ τ P(90°) data shown in Figures 26 through 33.

N. DENSITY OF THE CF₃NO/C₂F₄ COPOLYMER GUM

Densities were measured by a displacement technique in a low viscosity silicone fluid. The average density of samples XP5675 and XP5702 was 1.937 ± 0.001 g/cc at 25°C.

O. QUALITATIVE AND QUANTITATIVE ANALYSIS OF CONTAMINANTS IN PRODUCTION LOTS OF CF₃NO/C₂F₄

Insoluble gels from 25-50% (in FC-75) plus a white insoluble material were present in the Thiokol CF₃NO/C₂F₄ samples. The white insoluble substance varied from 1-3% by weight of the sample.

The IR spectrum of the white insoluble material removed from sample XP5702 is shown in Figure 34.

Emission analysis was also performed which indicated the presence of magnesium.

The unfractionated specimens contained 15-20% by weight of a relatively volatile high viscosity liquid which could be removed by vacuum drying or just heating (see Figure 20 for example). A specimen of the volatile material was removed from Thiokol sample XP5702. The infrared spectrum of this material is shown in Figure 35, and the NMR F¹⁹ spectra are shown in Figure 36. An attempt to observe spin-spin coupling was attempted by diluting the volatile material with CFC1₃. No improvement in resolution over that shown in Figure 36 was observed.

A proton resonance NMR was conducted with negative results.

P. LINEAR THERMAL EXPANSION OF THE CF₃NO/C₂F₄ COPOLYMER

"Apparent" linear thermal expansions were determined on the CF₃NO/C₂F₄ gums from -75°C up to their glass transition (T_g). Samples XP5702, XP5812, XP5887, and a vacuum-dried sample XP5675 were evaluated. The tests were conducted at a temperature heating rate of 1°C per minute introducing a dynamic nature to the standard ASTM D696-44 technique. For this reason the word "apparent" is attached to the title. A quartz dilatometer was utilized for the measurement.

The glass transition temperatures, T_g , were determined by the temperature at which $\left(\frac{\partial \Delta L}{\partial T}\right) = 0$.

A typical linear thermal expansion curve is shown in Figure 37 for sample XP5702 and the "apparent" linear thermal expansion coefficients and their extrapolated T_g 's are shown in Table 6.

Q. 1000 CYCLES PER SECOND MODULUS BY REBOUND METHOD OF THE CF_3NO/C_2F_4 GUM

Figure 38 shows the rebound tester used to determine the glass transition of a material at 1000 cps by measuring the rebound of a small (1/8 inch diameter) ball bearing from the surface of a specimen. Although complete correlation has not been made, the percent rebound as measured by the instrument has been shown to correlate to the logarithmic decrement of a material (Ref. 5). Since the logarithmic decrements goes through a maximum where the elastic modulus decreases rapidly from a glassy state to a rubbery state (i.e., the glass transition), we may roughly predict the glass transition temperature at 1000 cps.

The need for such a test is a result of the inability to obtain any reasonably shaped or geometrically stable specimen. The rebound test requires only a flat non-sticky surface. The tackiness of the nitroso gum is no problem at low temperatures; however, from 0°C and up (where tackiness is a problem) an aluminum surface can be used without altering the position of the transition region (only magnitude, of relative importance only, is affected).

Data of percent rebound versus temperature for specimen XP5675 are reported in Figure 39. A 0.5 mil aluminum foil covering was attached to the gum as a rebound surface, and the specimen was tested from -100° to 40°C.

R. AMINE DEGRADATION OF THE CF_3NO/C_2F_4 GUMS

The degradative effects of cyclohexylamine and n-butyl amine refluxed over the XP5702 sample of CF_3NO/C_2F_4 were determined. The analysis was conducted by measuring

the solution viscosity of the gum prior to and after refluxing with the amines for a period of time. The refluxing times were dictated by the work of the 3M Company previously reported (Ref. 6).

The results are recorded in Table 7. The intrinsic viscosities and molecular weights are calculated from the specific viscosities. The gums were also aged in FC-75 and FC-43 at 50°C with no measurable change in viscosity with time.

S. FORMULATIONS AND CURE CONDITIONS OF AMINE-CURED
CF₃NO/C₂F₄ COPOLYMER

1. Rubber Product

In order to provide a CF₃NO/C₂F₄ rubber for characterization, a minor effort in formulation and curing was conducted. The original formulations were based upon the reported data of the 3M Company and the U.S. Army Natick Laboratory (Ref. 1 and 2). The basic formulation consisted of:

	<u>Weight</u>
CF ₃ NO/C ₂ F ₄ gum	100.00
SiO ₂ filler	15.00
Triethylenetetramine	1.25
Hexamethylenediamine carbamate	2.50

The lack of success in producing a rubber with properties similar to those reported by 3M and the 3M and the Natick Labs resulted in alterations to the basic formulations and a short curing study involving the ADL ball rebound tester.

The CF₃NO/C₂F₄ formulations and curing procedures are shown in Table 8 where the XP5812 (purified), XP5702 (purified), XP5887, and Peninsular ChemResearch bulk-polymerized (purified) gums were utilized.

The details of the milling and molding of the numerous batches were reported earlier (Ref. 7 and 8 and in Appendix F). Relatively standard rubber technology was utilized.

2. Adhesive Product

Five master batches were used to determine the utility of the $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ rubber as an adhesive. The stainless steel strips were prepared by the procedure outlined in Appendix G. The bonding procedure used was as follows:

- a. 1 g of the sample was placed between two overlapping strips (1" x 1/2" overlap area).
- b. The samples were placed in a press, pre-heated to 212°F.
- c. After 5 minutes in the press, 225 lb (gage) pressure was applied to the samples.
- d. The samples were left at 212°F and 225 lb (gage) pressure for 1 hr.

After pressing, only two of the samples, (37593-1 and 37593-2), held a bond. These samples were then post-cured in an oven at 122°F for 16 hours, at 167°F for 2 hours, at 212°F for 72 hours, and at 239°F for 2 hours. The strips were then pulled apart at a crosshead speed of 0.05 inches/min. Instrument failure caused no recording of load for sample 37593-1. Sample 37593-2 had a strength of 180 psi. In both cases, the failure was cohesive.

3. Amine-Curing Studies Utilizing the ADL Ball Rebound Apparatus

Portions of the "Master Batches" that gave somewhat favorable results on the tensile tests were milled to a thickness of about 5.5 mils. From these milled samples, 1/2-inch diameter specimens were cut for the ball rebound apparatus (see Figure 38). Test temperature started at 74°F on the uncured gum and was increased to 230°F.

Shore A-2 durometer readings were taken on the samples before and after test. The results are recorded in Table 9.

Figure 40 shows the data for rebound versus temperature of samples 37593-1A, 37593-2A, and 52905-1A (see Table 8). These three samples have the same $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ gum and amines, both type and amount. They vary in type and content of fillers: 37593-1A has 15 parts HiSil 101 and no MgO ; 37593-2A has 15 parts HiSil 101 and 10 parts MgO ; 52905-1A has 7.5 parts HiSil 101 and 7.5 parts MgO .

Figure 41 illustrates the rebound versus temperature data for samples 52911-1A and 52911-2A (see Table 8). These two samples have the same type and quantity of nitroso gum and fillers, varying in the type and quantity of amines: 52911-1A contains 1.25 parts TETA and 2.5 parts Oxydianiline; 52912-1A contains 0.65 parts TETA and 2.5 parts HMDAC.

Figure 42 shows the rebound versus temperature data for samples 52912-1A and 52912-2A (see Table 8). These two samples vary only in type of nitroso gum; 52912-1A contains Peninsular ChemResearch (purified) gum. Both of these samples "sponged" during the test.

T. PHYSICAL MECHANICAL PROPERTIES OF THE AMINE-CURED $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ RUBBER

1. "Static" Tensile Properties

The tensile strengths (ultimate, stress at 100% elongation and at 300% elongation), ultimate elongation, and hardness values for the various amine-cured $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ rubbers are shown in Table 8.

The tensile tests were conducted on micro-tensile specimens with a one-inch gage length. Crosshead rates of 20 inch per minute were utilized throughout. The hardness measurements were conducted on the Shore A apparatus.

2. 1000 Cycles Per Second Rebound Modulus

The 1000 cps modulus for the uncured nitroso gum has previously been determined by the rebound technique (see Section Q). The 1000 cps modulus of cured samples 37559-4 and 37559-5 is shown in Figure 43. The rebounding

occurred from the surface of the rubber specimen as opposed to the technique of rebounding from an aluminum foil surface layer, as was necessary for the tacky gums.

3. 3 Cycles Per Second Forced Torsional Pendulum Modulus

Using a modified Nonius Torsion pendulum, as shown in Figure 44, the 3 cps loss modulus of samples 37559-5 and 37559-8 was determined. The torsion pendulum is modified by replacing the fine supporting wire with a rigid steel rod. The rigid rod provides a driving force that maintains the frequency of test at approximately 3 cps and allows testing lower modulus values, which a normal torsion pendulum, due to the required support of the specimen, would not allow. Because the damping values are of the steel-rubber composite system, they cannot be related to modulus terms developed merely on material properties. The temperature of maximum damping, however, is real and meaningful. The damping of rubber samples 37559-5 and 37559-8 is shown in Figure 45.

4. Clash-Berg Torsional Modulus

The torsional modulus (static) by the more standard technique of Clash-Berg is shown in Figure 46 for rubber sample 37559-5. T_g (modulus at 4500 psi) is at -49°C , and T_{665} (modulus at 665 psi) is at -32.5°C . This provides a Stifflex range of 16.5°C with a midpoint of -40.8°C .

5. Metal-to-Metal Adhesive Shear

The procedure and results of these few tests are reported in Section S.2. The cohesive failure amounted to a strength of 180 psi.

U. SOLVENT AND CHEMICAL RESISTANCE OF THE AMINE-CURED $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ RUBBERS

Sample 37566 - Cure No. 1 was molded into a 4" x 4" x 0.02" sheet. Specimens approximately 2" x 0.38" x 0.02" were cut from this sheet. Their weights and volumes

were determined and the specimens were placed in the 14 solvents and chemicals shown in Table 10. The weights and volumes of the specimens were redetermined at various intervals up to a total of 1128 hours. These and the calculated densities are shown in Table 10 with the corresponding solvent density. Also shown in Table 10 are the results of cure sample 37559-8 immersed in FC-75 up to 1412 hours. This amine-cured, SiO_2 -filled rubber had exhibited a tensile strength of 267 psi and 420% elongation.

The viscosity of the FC-75 solvent was measured to determine if the polymer was being extracted. No significant change was noted.

The swelling of sample 52905-1-1, 52911-2-1, 52912-1, and 52912-2-1 in FC-75 for periods up to 1200 hours is shown in Table 11. The percent weight and volume change from original is reported versus time.

V. THERMOGRAVIMETRIC ANALYSIS OF THE AMINE-CURED $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ COPOLYMER

TGA in helium and in air was conducted on the amine-cured rubber XP5675, the results of which are shown in Figure 47. In air, the rubber violently decomposed at 270°C , forcing the remainder of the specimen out of the weighing crucible.

IV. DISCUSSION

A. SOLVENTS FOR THE CF₃NO/C₂F₄ COPOLYMER

The attempt to provide solvents consisted of finding the best solvents available so that solution studies could be performed. Naturally, solubility, per se, would be the primary factor in choosing a solvent. However, due to the generally poor solubility of CF₃NO/C₂F₄ in any solvent and because of the increased ease (decrease in time) with which a gum can be put into solution at elevated temperatures, a solvent with a relatively high boiling point was preferred. A solvent that is a liquid at room temperature also was considered to be an advantage.

Since Freon 112 melts at room temperature, it, therefore, would not have been convenient to use.

FC-43 exists as a liquid at room temperature and has a boiling point at 170-180°C, thus making it a convenient solvent. However, periods ranging 2 to 3 hours at 100°C were necessary to dissolve the polymer in this solvent.

FC-75 also exists as a liquid at room temperature, having a boiling point near 100°C. In addition, dilute solutions of the rubber gum could be prepared in less than 30 minutes at 100°C.

Freon 113 is a liquid at room temperature and boils near 45°C. Dilute solutions of the rubber gum could be prepared in 2 hours with moderate heating.

The utility and convenience of the solvents would thus place them in the order: (1) FC-75, (2) Freon 113, (3) FC-43, and (4) Freon 112.

Other Freons exhibit such a narrow range between their melting and boiling points along with such low boiling points, that they were not considered.

No really good solvent was found for the CF₃NO/C₂F₄ copolymer, as shown by the solution viscosity measurements (see Section C).

B. FINGERPRINTING OF THE $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ COPOLYMER BATCHES

The original scope of the characterization program assumed that numerous production samples of the $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ gum would be submitted. Additionally, it was considered that these samples would be quite similar or identical and therefore could be represented by just one of the batches. A simple fingerprinting procedure was thus considered to be desirous in order to rapidly determine the similarity of the batches.

Solution viscosity measurements in two different solvents were originally proposed as the technique for fingerprinting and, as shown in Figures 1 and 2, could easily distinguish the differences between three of the gums. Such an analysis would distinguish a difference in molecular weight and molecular weight distribution for a given copolymer. It, of course, could not describe the weight distribution, other than to show that a difference existed.

The difference between submitted batches, however, was so extreme, as shown by the viscosity data, that such a refined procedure was not necessary to show that differences did exist.

A simpler technique, therefore, that did not require causing solution or forming of a specimen, was devised utilizing the Vicat (ASTM D1525-58T) indentation as a function of temperature. As shown in Figures 3 through 5, the various batches were easily distinguished as being different by their Vicat temperature (temperature at 1 mm indentation) and the slope of the indentation curve.

Figure 6 demonstrates the utility of the Vicat technique to show that one of the significant differences between the batches was the presence of differing amounts of volatile portion that could be removed by vacuum drying.

The Vicat temperature was also an excellent indicator of the relative glass transition temperatures. The lower Vicat temperatures of the Peninsular ChemResearch samples were probably significant and an indicator of an idealized gum.

C. SOLUTION VISCOSITIES

Solution viscosities were determined in the solvents FC-75, FC-43, and Freon 113, with major emphasis being placed upon the FC-75 solvent discussed in Section A. The low intrinsic viscosities and corresponding shallow slope of the reduced viscosities versus concentrations shown in Figures 1, 2, and 7, indicated the relatively poor solubility of the $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ gum in these solvents. The solubility of the gum in the FC-75 solvent was also shown to be the best.

The intrinsic viscosity is related to the reduced and inherent viscosities by the Huggins equations:

$$\eta_{sp}/C = [\eta] + K'[\eta]^2C$$

$$\text{and } (\ln \eta_r)/C = [\eta] - K''[\eta]^2C$$

where theoretically $K' + K'' = 0.500$.

The K' , K'' , and $K' + K''$ determined for two of the representative samples of $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ gum in the three solvents were:

Solvents	XP5675			XP5702		
	K'	K''	$K' + K''$	K'	K''	$K' + K''$
FC-75	0.366	0.138	0.504	0.396	0.124	0.520
FC-43	0.316	0.172	0.488	0.422	0.109	0.531
Freon 113	0.086	0.363	0.499	0.009	0.417	0.426

In cases where sample was sufficient only to measure specific viscosity, the intrinsic viscosities were calculated utilizing the above K' and K'' values (see for example Tables 3, 4, and 5).

The K' and K'' constants were rigidly defined for the $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ copolymer, utilizing clean fractions of sample XP5702 in FC-75. The K' and K'' constants for the $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ in FC-43 and Freon 113 were not determined on as pure fractions of gum, and therefore may have to be slightly revised. The primary difficulty lay in selecting what would be considered an idealized or representative $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ sample. As discussed in Section D, sample XP5702 was arbitrarily selected.

The main difficulty in measuring solution viscosities, besides the problem of no really good solvents being available, was the cleaning of the submitted gums. The gums contained 25% to 50% insoluble gels and particulate matter plus 20% volatile (low boiling) gum. Causing solution and measuring viscosities at elevated temperatures could possibly decrease the amount of insoluble gel; however, the volatile portion of the sample would be lost. Because the insoluble gels remained as an exceedingly tacky substance that collected in filters, frits, and on glass, they could not be readily recovered.

The Peninsular ChemResearch bulk and solution-polymerized $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ samples also contained the insoluble gels and volatile material.

D. ELEMENTAL ANALYSIS

The C, H, N, F, and O (by difference) analysis was performed on four of the Thiokol-submitted samples and the two Peninsular ChemResearch $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ samples. This analysis was conducted upon receipt of the samples, at an interim period, and also after the samples had aged in the standard laboratory atmosphere for a year and a half.

Also calculated was the deviation from theoretical, "Atypicality", of each of the samples. The closer the Atypicality value is to zero, the closer the analysis is to theoretical. The significance of the atypicality analysis is that (1) if an impurity alone were volatilizing away, the atypicality would decrease as the atypical contaminant was removed; (2) if monomer is volatilized due to depolymerization or incomplete conversion, the material remains unchanged or increases in atypicality, depending upon whether or not comonomers are lost at the same rate.

The atypicality of the sample XP5675 did increase during a six-month period and could not be explained by the loss of any known fluorinated solvent or apparent decomposition. We would suggest sampling as the real difference. Over the 1-1 1/2 years, however, the atypicality decreased, indicating a loss of some nontypical material.

The vacuum drying of sample XP5702 decreased the Atypicality of the gum, indicating that impurities, possibly monomeric material, existed in the volatile portion of the gum.

In all cases the Atypicality decreased with time, signifying that the impurities were a volatile substance, or at least combined to give the theoretical structure (less likely). The inability to determine oxygen content separately in the presence of fluorine limited our ability to completely analyze the situation.

The Peninsular ChemResearch samples showed excellent typicality as compared to the Thiokol samples.

Because of the larger sample available, the relatively low atypicality, and the proven ability to reduce atypicality by vacuum drying, the purified XP5702 gum was selected as the typical gum for this characterization program.

E. INFRARED ANALYSIS

Infrared spectra in the 2-15 μ range were determined on samples XP5675, XP5702, XP5812, XP5887, and 3M - 56703-3. They are represented by the spectra shown in Figures 9 and 10.

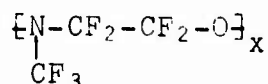
Strong C-F stretching vibrations show up at 1153, 1245, and 1300 cm^{-1} with weak overtones near 2400 cm^{-1} . The peak at 830 cm^{-1} is believed due to $\text{-CF}_2\text{-CF}_2\text{-}$ bend, and the one at 745 cm^{-1} either to $\text{-CF}_2\text{-CF-}$ or -CF-CF- , neither of which appear in the idealized averaged structure obtained by NMR (see Section F). The absorptions at 1065 and at 1103 cm^{-1} are assigned to C-O-N stretching; the weak to medium absorptions at 2010, 2085, 2400, and 2530 cm^{-1} appear to be first harmonics of the C-O-N and C-F stretching absorptions. These weak to medium bonds were not observed in sample XP5675, even though they are customarily seen in perfluorocarbon spectra.

The absence of hydrogen is noted, in that there are no bonds near 3000 cm^{-1} . Also, significantly, no $\text{-CF(CH}_3)_2$ at 730 cm^{-1} nor $\text{-CF}_2\text{CF}_3$ at 735 cm^{-1} were noted.

Sample XP5702 exhibits a spurious peak at 1735 cm^{-1} in the region normally assigned to saturated non-fluorinated esters and aldehydes, α -halogen ketones, and α -halogen acids. The most likely explanation, considering the slight brownish color of the sample, is that overtemperature at some point in the processing allowed some trace oxidation or rearrangement to halogenated ketones and acids.

F. NUCLEAR MAGNETIC RESONANCE ANALYSIS

Shown in Figure 11 is the NMR spectrum obtained for sample XP5675. The spectra for the remaining samples were almost identical, although small deviations were noted in exact peak location and height. Listed in Table 12 are these peaks and their assignments. The structure defined is:



Attempts were made to provide better resolution and possibly a more detailed structure or indication of some anomaly. The high viscosity of the solutions and poor solubility of the polymer prevented any further detailed analysis of the whole gum. See also Section O for a description of the volatile portion of the gum.

G. X-RAY ANALYSIS

The presence of only diffuse diffraction patterns from -70° to 28°C indicated no crystallinity.

H. MASS SPECTROGRAPHIC ANALYSIS

In an attempt to establish the nature of the volatile portion of the $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ gums submitted by Thiokol and to confirm the mode of thermal decomposition of the gum, mass spectrographic analyses were conducted isothermally from 23°C to 275°C in 50°C intervals.

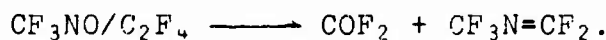
Figure 13 shows the existence of the volatile which starts evolving at 50°C, reaches a maximum at 100°C, and continues to be evolved above 200°C (below the decomposition temperature). The removal of this volatile portion was demonstrated on a vacuum-dried fraction which, following the expected thermal decomposition nature of a gum with a single distribution of molecular weights, started decomposing at 150°C, proceeded through a maximum at 250°C and continued to decompose the various molecular weight components up to 500°C. The volatile portion thus has the nature of a nitroso gum of low and normally distributed molecular weights.

Knowing the nature of the volatile product, the isothermal mass spectrographs should have determined the make-up. If solvents or other contaminants were present, it would be expected that these would be shown as evolving at temperatures in the volatile region, adding to those masses expected for the nitroso copolymer. The results of the mass spectrographic data indicated that there were no, even slightly significant, different masses given off in the volatile region and that the products given off in the volatile region were identical to those at elevated temperatures. The most prominent masses given off by the nitroso copolymer are those shown in Figures 14 through 19. The most probable species to associate with those masses are listed in Table 13.

It should be noted that mass 100, which is associated with C_2F_4 , is not present with the ratio of component masses which indicate tetrafluoroethylene. The C_2F_4 is a result of an ionic species created by the mass spectrograph from the polymer chain.

Figures 14 through 19 show that the XP5675, the vacuum-dried XP5675, and the 3M - 36703-3 do not differ in their composition. The difference in intensities is a function only of the molecular weight distribution.

We had also hoped to show that the mode of decomposition was, as shown by Shultz, *et al.* (Ref. 9):



This would be shown on the mass spectrographic data by an increase in masses 66 (COF_2) and 133 (CF_3NCF_2). Mass 66 did increase as expected (see Figure 14 for example); however, a corresponding increase in mass 133 was not demonstrated. The nature of the CF_3NCF_2 spectra is not known, but a further break up of this portion could account for the lack of the mass 133 increase. Even though the data probably confirm the expected decomposition mode, it cannot establish it.

I. THERMOGRAVIMETRIC ANALYSIS

Shown in Figures 20 and 21 is the thermogravimetric analysis curve obtained from a 0.100 g sample of gum under vacuum (0.3 mm Hg) when heated at a nominal $3^\circ\text{C}/\text{minute}$. Beginning at $\sim 75^\circ\text{C}$ a very gradual weight loss occurred up to $\sim 260^\circ\text{C}$. At this point, an extremely rapid loss occurred. A downward thrust was exerted on the sample crucible. A sharp spike appeared in the weight-loss curve, and this spike was found to be highly reproducible. By 350°C , the entire sample had dissociated, leaving no residue. Shultz, Knoll, and Morneau (Ref. 9) confirmed this unzipping by the use of differential thermal analysis, noting exactly the same temperature for the beginning of the reaction.

Vacuum-drying of a sample demonstrated that the initial loss was due to a volatile product and that the actual decomposition occurred at 260°C .

The composite isothermal thermogravimetric data shown in Figure 22 are most significant. A leveling-off of weight loss occurred at each temperature indicating that each weight loss is associated with a particular molecular weight fraction. No breaking-down of higher molecular weight fractions occurred that would produce shorter chain fractions which could then be lost (confirmed also by the mass spectrographic data).

A comparison of the thermal decomposition of the $\text{CF}_3\text{NC}/\text{C}_2\text{F}_4$ copolymer in air and in an inert gas indicates no effect of oxygen upon the thermal failure.

In both cases, a volatile portion (which has been shown to be removable) is evident from 50°C to 200°C with a peak at 100°C. Primary decomposition occurs at 260°C (from 150°C to 350°C).

No violent decomposition occurred during decomposition of a relatively small specimen.

J. DIFFERENTIAL THERMAL ANALYSIS

As shown in Figure 23, the glass transition by DTA of the $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ copolymer was located in the region of -41° to -46°C. The transitions of the three samples, 3M-56703-3, XP5675, and XP5702, are within 2°C of each other. The DTA method does not allow for further refinement of the difference in the transitions of the various samples. The change in slope in the region of -51° to -56°C of sample XP5702 is undefined, and it is, at present, doubtful if it is real or not. The possibility of this being the lower-molecular-weight gum is considered, but has not been proven or entirely anticipated. X-ray analysis shows that it is not crystallinity (see Section G). The various slopes shown in Figure 23 are probably more a result of the technique than a characteristic of the polymer. The change in slopes, however, is real and has been confirmed by repeated analyses.

High temperature DTA confirms the decomposition temperature of ~260°C established by thermogravimetric analysis.

K. SOLVENT/NONSOLVENT SYSTEMS FOR THE $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ COPOLYMERS

In order to obtain the molecular weight fractions of the nitroso copolymer, a solvent/nonsolvent system is necessary. Once such a system is determined, a means of fractionating may be employed, such as solvent/nonsolvent precipitation or elution fractionation.

Four useful solvents had previously been selected (see Section A). Of these, two were selected on the basis of useful boiling points (less than 100°C), being relatively nonviscous, and having a miscible nonsolvent with similar properties.

The FC-43 $[(C_4F_9)_3N]$ was too viscous (2.8 cs) and has a boiling point of 170°C. The Freon 112 does not melt or flow to temperatures of 25°C; therefore, it is most unsuitable as a fractionating solvent.

The Freon 113/acetone, solvent/nonsolvent, system has been reported previously by others (Ref. 1). It is very good with the exception that the higher molecular weight nitroso portions are difficult to get into the Freon 113 solvent. The boiling point of 50°C also limits the temperature range usable to aid in separation of the fractions (by improving solubility).

The utility of the FC-75/benzotrifluoride system was demonstrated (see Table 2 in Section L). A range of 40°C is available between the condition when the polymer is all in solution and when it is all precipitated out. A ratio of almost 1:1 of the two solvents before the gum is out of solution allows for a broad range of solvent ratios available for removal of the fractions from the elution column. The sensitivity of the gum solution to temperature and solvent ratio is high, however, so that great care is required in preparation of the fractions.

L. FRACTIONATION OF THE CF_3NO/C_2F_4 COPOLYMER BY THE ELUTION TECHNIQUE

Fractionation was performed by selective deposition of the polymer from a solubility-critical solution of FC-75 and benzotrifluoride. Deposition occurred upon cooling from 78°C to ambient and evaporation of the solvent mixture. Complete removal of all of the mixed solvent from the elution column was found necessary to prevent premature removal of the polymer by the nonsolvent flush. Overnight drying by flushing with dry nitrogen gas was found adequate to remove the solvent mixture. 1.5 grams of polymer was deposited in this manner.

Depending upon the quantity of material desired in each fraction removed, 1% to 2% solvent/nonsolvent increments are recommended. Increments of 2% provide fractions adequate for viscosity and light scattering determinations, whereas 1% increments provide only

sufficient quantities for point viscosity determinations that are required to specify a weight-viscosity distribution. Increments of 5% were found to cause nonselective elution, resulting in viscosity reversals in the expected higher viscosity regions (Ref. 8).

An elution temperature of 56.6°C was found to allow more selective elution fractions than did a 78°C elution temperature.

Elution solvent/nonsolvent ratios from 35% to 55% removed 95% of weight of the polymer. Approximately 6% low-molecular-weight material was removed with the non-solvent flush, and all but a fraction of a percent of the polymer was removed by the pure solvent.

Up to 25 fractions of the XP5702 polymer were recovered in the above manner, using 1% solvent increments (see Tables 3, 4, 5). The XP5702 polymer fractionated in this manner had been purified previously by filtering out at least 25% gel. The removal of this gel is a tedious, but necessary, procedure. The gel was not collected in a manner that would allow its characterization.

The viscosities of the fractions eluted by 1% solvent/nonsolvent increments were determined in FC-75 at 0.1% concentration. The integral and differential weight-viscosity distributions of two purified samples of XP5702 and the PCR-bulk-polymerized copolymer are shown in Figures 24 and 25.

The differential weight-viscosity distribution shows two separate dominant viscosity portions. The two portions have reduced viscosities of ~ 0.2 and ~ 2.3 . The 2.3 viscosity region, however, is most dominant. The nonsymmetry of the weight distribution about the higher viscosity portion is due to the presence of the lower viscosity polymer portion and slight viscosity reversals in the fractionation. It is in all probability real, due to the unusual polymerization process encountered in the formation of the polymer. Fractionation of the polymer with the low viscosity portion removed would be required to establish the reasons for the lack of symmetry normally not encountered in polymer distributions.

The similarity of the weight-viscosity distribution to the weight-loss temperature (TGA) spectrum shown in Figure 22 is noteworthy. The TGA curve indicates that the low viscosity portion contributes significantly to the nonsymmetry of the polymer weight distribution.

The fact that the reduced viscosities of the various portions are identical at 35°C to those measured at 25°C (see Table 3) proved that determinations were not conducted in a critical solubility region of the CF₃NO/C₂F₄-FC-75 solution.

M. MOLECULAR WEIGHT DETERMINATIONS AND DISTRIBUTIONS OF THE CF₃NO/C₂F₄ COPOLYMERS

Light-scattering measurements were performed on four CF₃NO/C₂F₄ copolymer samples, including the 3M - 56703-3 gum, fraction no. 4 of fractionation run 2 XP5702, fractions 13 and 14 of fractionation run 3 XP5702, and fraction no. 15 of fractionation run 3 XP5702 (see Tables 4 and 5).

The light-scattering Zimm plots are shown in Figures 26, 28, 30, and 32, and the Hc/τ P(90°) data are shown in Figures 27, 29, 31, and 33.

The weight average molecular weights were calculated by means of the Debye equation,

$$\frac{32\pi^3 n^3 (dn/dc)^2}{3N_o \lambda^4} \frac{C}{\tau} = \frac{Hc}{\tau} = \frac{1}{M_w P(\theta)} + 2A_2 c + \dots$$

where for FC-75 n^2 = refractive index of solvent = (1.281)

dn/dc = refractive index increment of solution = 0.025

λ = wavelength of light used = 4360 Å

N_o = Avogadro's number = 6.02×10^{23}

A_2 = Osmotic second virial coefficient

$P(\theta)$ = scattered light intensity.

The index of refraction for FC-75 supplied by 3M is credited to E. F. Beale, University of Maryland. The equation for the refractive index as a function of wavelength is:

$$n = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}$$

where $A = 1.2777$
 $B = -6.4 \times 10^{-5} \mu^2$
 $C = 1.3 \times 10^{-4} \mu^4$

The refractive index of FC-75 varies from 1.294 to 1.278 between 2800 Å and 6000 Å.

The value of dn/dc found was 0.025, determined with a Brice-Phoenix differential refractometer. No fluorescence was evident. Dissymmetry was corrected by two methods - Zimm plot extrapolation to zero concentration and angle where $P(\theta) = 1$, and by Debye's original method of direct measurement and correction for dissymmetry of scattering, due to molecular dimensions that are large compared to λ . The solvent FC-75 at 25°C is apparently close to being a critical consolute solvent (no polymer-solvent interaction), as a number of the Zimm plots were long and narrow with sufficient scatter-uncertainty as to render it of dubious value for molecular weight or end-to-end chain length determinations.

In particular, the Zimm plots of the samples 3M - 56703-3 and XP5702 - Run 3 - f15 were not usable. Guided by the $H_c/P(90^\circ)$ plots, the Zimm zero concentration-angle extrapolations were reasonable for samples XP5702-R2-f4 and XP5702-R3-f13,14. However, all reported M_w values were obtained by zero concentration extrapolation of $H_c/P(90^\circ)$.

The particular Brice-Phoenix light-scattering instrument utilized was checked with an NBS polystyrene. The determined M_w was 5% higher than that reported by NBS. No corrections were made to the M_w data reported herein; however, consideration should be given to this difference as a possible correction.

The molecular weights determined for the four samples and the corresponding intrinsic viscosities in FC-75 at 25°C are:

Sample	$[\eta]$	\overline{M}_w
3M-56703-3	0.42	0.56×10^6
XP5702-R2-f ⁴	1.30	1.8×10^6
XP5702-R3-f ^{13,14}	1.15	3.3×10^6
XP5702-R3-f ¹⁵	1.69	3.9×10^6

These data are shown in Figure 48 relating the intrinsic viscosity of the $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ copolymer in FC-75 to molecular weight.

These data may be expressed by the Mark-Houwink equation:

$$[\eta] = K \overline{M}_w^a$$

Utilizing the data, the values of K and a are:

$$\begin{aligned} K &= 3.2 \times 10^{-5} \\ a &= 0.72 \end{aligned}$$

These constants may be compared with the values of Morneau et al. (Ref. 1) for FC-73 and Freon 113.

	$T, ^\circ\text{C}$	K	a
Perfluorocyclic ether (FC-75)	25	3.2×10^{-5}	0.72
Perfluorotributylamine (FC-43)	25	8.77×10^{-5}	0.60
Trichlorotrifluoroethane (Freon 113)	35	3.80×10^{-5}	0.71

Utilizing the Mark-Houwink K and a constants, the viscosity weight distributions shown in Figures 2⁴ and 2⁵ may be approximated as molecular weight total and differential distributions. The calculated \overline{M}_w values are listed in Tables 3, 4, and 5. The \overline{M}_w , \overline{M}_n , and $\overline{M}_w/\overline{M}_n$ were determined for XP5702-R3, XP5702-R⁴, and the PCR-bulk-polymerized fractionated gums as described in Appendix D. The values are:

<u>Sample</u>	<u>M_W</u>	<u>M_N</u>	<u>M_W/M_N</u>
XP5702-R3	3.4 x 10 ⁶	2.7 x 10 ⁴	125.
XP5702-R4	3.4 x 10 ⁶	1.9 x 10 ⁵	18.
PCR-bulk Plyz.	2.0 x 10 ⁶	2.3 x 10 ⁴	88.

The presence of a sizable low-molecular-weight portion was shown in all cases as was noted by Morneau, *et al.* (Ref. 1) for the 3M-produced gums. This low-molecular-weight portion strongly weights the M_N of the whole gums, causing M_W/M_N ratios to be considerably higher than normal.

N. DENSITY OF CF₃NO/C₂F₄ COPOLYMER GUM

The density of the CF₃NO/C₂F₄ gum is high with a value of 1.937 ± 0.001 g/cc.

O. QUALITATIVE AND QUANTITATIVE ANALYSIS OF CONTAMINANTS IN PRODUCTION LOTS OF CF₃NO/C₂F₄

Analysis of the IR data and the emission analysis shows that the white insoluble material was a mixture of CF₃NO/C₂F₄ gum similar to XP5675 and basic magnesium carbonate trihydrate (Satler #1740).

The assignments given to the absorption bands of the infrared spectrum are (see Figure 34):

Sample XP5702 IR Assignments

<u>(microns)</u>	<u>Assignment</u>
2.9 } 6.1 }	H ₂ O
7.7 } 7.0 }	Carbonate ion
7.7 } 8.0 } 8.7 } 9.1 } 9.4 } 9.75 } 10.9 }	Nitroso rubber

Sample XP5702 IR Assignments

<u>(microns)</u>	<u>Assignments</u>
11.3 } 11.7 } 12.5 }	Basic magnesium carbonate trihydrate
13.5 } 14.2 }	Basic magnesium carbonate trihydrate and nitroso rubber

In some samples, this amounted to 3% by weight contaminant.

A sample of the volatile high viscosity liquid was examined by NMR and IR (see Figures 35 and 36). The peak groups were observed that occurred in the spectral regions previously assigned to $-CF_3$, $[OCF_2]CF_2-$, and $[NCF_2]CF_2-$. There were at least two different magnetic environments for each peak group. Unfortunately, the line width of the peaks was too great to permit resolution of the subsplitting that resulted from spin-spin interactions. The poor solubility of the polymer excluded improved resolution macro techniques.

The multiplicity in each peak group is believed to result from the influence of the β groups. As a general rule, $-O-$ has a greater effect, i.e., produces a greater displacement of resonance to lower field, than does $-NR_2$. Although there are no positive indications of any measurable amount of $-NO_2$ (see Figure 35), the β effect of this group is much greater than the $-O-$ or $-NR_2$ groups, and would produce an even greater displacement to a lower field.

Note the relative peak group areas, and the relative peak heights and shapes on each peak group. There is no indication of the presence of $-CF_2(CF_2)_nCF_2-$.

P. LINEAR THERMAL EXPANSION OF THE CF_3NO/C_2F_5 COPOLYMER

Apparent linear expansion coefficients were measured on the various gums with the most typical gum (theoretically) exhibiting a value of $7.6 \times 10^{-5}/^\circ C$ from $-72^\circ C$ to the glass transition temperature. The more typical production gums exhibited a change in their expansion coefficients between $-72^\circ C$ and their glass transition temperature.

The glass transition temperature (expansion coefficient method) for the most typical nitroso gum was -49°C . Other gums varied from -46° to -48°C (after vacuum-drying).

The change in expansion coefficients was probably due to the varying amounts and presence of the low molecular weight gum.

Q. GLASS TRANSITION OF THE $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ COPOLYMER GUM AT 1000 CYCLES PER SECOND BY REBOUND METHOD

Figure 39 shows the minimum rebound (maximum loss) to be in the region of -18°C . This is the 1000 cps glass transition temperature. Using an equivalence of 7°C per decade of frequency (which is an approximation), the 0.1 cps glass transition (such as determined by the torsion pendulum) would be -46°C .

This test and temperature provide a reasonable result, especially since other dynamic tests are not usable on gum stocks.

R. AMINE DEGRADATION OF THE $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ GUMS

The degradation of the $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ copolymer by refluxing amines was performed to determine the similarity to the 3M copolymer (Ref. 6) studies. The similarity was confirmed, and it was shown that all molecular weight species were degraded to a similar low level during a one-hour refluxing with cyclohexylamine. Molecular weights were reduced from as high as 6×10^5 down to 8×10^4 .

A significant problem of curing with amines, as had been expected, was confirmed.

S. FORMULATION, CURE CONDITIONS, AND MECHANICAL PROPERTIES OF AMINE-CURED CF₃NO/C₂F₄ COPOLYMERS

1. Rubber Product

The formulation and curing work on the nitroso gums was accomplished in four steps.

- a. Evaluation of the Thiokol XP5812 in the "standard" formulation.
- b. Evaluation of Thiokol XP5887 as to varying formulations and curing conditions.
- c. Maximization of Thiokol XP5887 by adjusting the formulation and curing procedure for best physical properties.
- d. Utilizing the best formulation and curing procedure found with Thiokol XP5887, preparing nitroso rubbers from (purified) Thiokol XP5702 and Peninsular ChemResearch nitroso gums, and comparing their physical properties.

a. Sample XP5812 was apparently a high-molecular-weight fraction as submitted, and was further washed with Freon 113 to remove possible low-molecular-weight fractions. Of those cured samples (see Table 8) (37559-1, 2, 3, 4, 5, 6, 7, 8), 37559-2, 3, 6, and 7, did not exhibit adequate physical properties to permit a mechanical test.

Sample 37559-2 had a yellow appearance, did not seem cross-linked, and probably had a strength of less than 100 psi. Sample 37559-3 seemed well cured, with a hardness of 30 (Shore A) prior to postcure and 33 after postcuring. Extreme blistering and porosity prevented adequate tensile tests. Sample 37559-6 turned dark brown during cure, indicating that degradation had occurred. Tensile strength (not measured) would have been well below 100 psi. Sample 37559-7 did not crosslink; however, the carbon black prevented the observability of any degradation. Its tensile strength would have been well below 100 psi, also.

The tensile strength, elongation, and hardness of samples 37559-1, 4, 5, 8 are shown in Table 8.

It was found that the cure cycle and postcure cycle had to be greatly modified in order to obtain adequate rubber. The cure was extended to 300 minutes at 250°F and the postcure applied in 30°F intervals for a period of one-hour each to 212°F, then held for 18 hours. Shorter cure times resulted in insufficient cross-linking, with the lack of stepped post-cure resulting in blistering and increased porosity.

The addition of a slight amount of Elastopar resulted in degradation of the gum during cure. Although no further studies were conducted, cures at lower temperatures may be possible. The use of carbon black as a filler was also found to be inadequate for reinforcing, preventing cross-linking. Even though the use of a higher-molecular-weight gum apparently improved the properties of the cured rubber, the results were not conclusive. Tensile strengths of 230 psi, 420% elongation, and a hardness of 39 were obtained with the amine-cured, SiO₂-reinforced XP5812 rubber. An additional improvement of 35 psi in strength and 8 Shore hardness units resulted from the addition of one-part of carbon black in the SiO₂-filled rubber. Thus a rubber of 267 psi tensile strength, 420% elongation, and 47 Shore A hardness units was obtained.

The temperature of maximum loss (minimum rebound), as determined by 1000 cps rebound modulus, was found to vary between -7° and -12°C for various amine-cured specimens (see Figure 43). The temperature of maximum loss for the 1000 cps modulus of the uncured gum had previously been determined to be -18°C.

The temperature of maximum loss as determined by 3 cps torsional pendulum modulus was found to be in the range of -41° to -44°C for the amine-cured rubber (see Figure 45). Relating the 3 cps modulus to the 1000 cps modulus would result in a translation of about 11°C per decade of frequency. This is a relatively high translation for a supposedly cross-linked rubber.

T_r (modulus at 4500 psi) as determined by the Clash-Berg torsional modulus was -49°C with a Stifflex range of 16.5°C (see Figure 46).

b. The best master batches of the five XP5887 gum type evaluated were 37593-1 and 37593-2. These two rubbers contained the same amines and amount of HiSil 101 filler. However, 37593-2 also contained 10 parts of MgO . Sample 37593-1 produced better elongation properties than did 37593-2 (480% to 270% for the latter), but 37593-2 produced better strength properties (350 psi for 37593-2 to 270 psi for 37593-1).

Sample 37593-3 differed from 37593-1 by containing 50 parts of HiSil 101 instead of 15 parts. This rubber was quite stiff in the uncured state, and very hard and brittle when cured. Each attempt to mold a sample of this rubber resulted with the molded disc cracking and breaking before it could be postcured. However, pieces postcured seemed to cure and hold together better as they were postcured.

Samples 37593-4 and 37593-5 were similar in appearance and properties. Sample 37593-4 was the same as 37593-1, except no amines were added. Sample 37593-5 was the same as 37593-1, except it had 6 parts of FC-43 amine instead of the amines used in 37593-1. Both of these rubbers were very soft and did not appear to be cured completely with use of the standard procedures that were used with samples 37593-1 and 37593-2.

c. The best results upon vulcanization were obtained from sample 52905-1 which contained 10 parts HiSil 101, 7.5 parts of MgO , 1.25 parts of TBT and 2.5 parts of BSAAC. This sample produced a tensile strength of 312 psi and an elongation of 540%.

Sample 52905-2 was produced in order to investigate the use of a carbon black instead of the HiSil as a reinforcer. This sample produced a tensile strength of 290 psi and an elongation of 473%. Further investigation of this system should be investigated. The results are better than over the carbon-black-filled 37593-1.

Sample 52911 had the same formulation as 52905-1 except 2.5 parts of Oxydianaline was used instead of 2.5 parts of HMDAC. The tensile strength and elongation were poorer than 52905-1. It also turned brown when cured.

Sample 52911-2 had the same formulation as 52905-1 except that only 0.65 parts of TETA was used, as compared to 1.25 parts in 52905-1. Poorer properties were obtained from this system. Further investigation should be made by increasing the amount of TETA in the 52905-1 formulation.

d. Sample 52912-1 (PCR's $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ gum) produced the best mechanical results (tensile strength, 387 psi; elongation, 527%). Sample 52912-2 (purified Thiokol XP5702) produced poor physical properties (tensile strength, 170 psi; elongation, 425%). The formulations for these two samples were the same as that used for 52905-1. Only the nitroso gums were different.

The fact that the PCR gum produced significantly better mechanical properties is significant. These properties, however, were still below those reported by 3M and the Natick Labs on earlier work (Ref. 2).

The best press cures employed varying temperatures rather than maintaining a stationary temperature.

It was also found that for best results, the press cure should only be used to obtain a molded sample with good surface qualities. The postcure should be used to obtain the best physical properties.

2. Adhesive Product

The same difficulties in providing a good cure, as with the rubber product, was observed in attempting to adhere metal to metal with an amine-cured $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ adhesive. The bond to the stainless steel was stronger than the rubber, as noted by the cohesive failures. The strength of the rubber, however, was only 180 psi. It was expected that this is a low value not necessarily characteristic of a well-cured rubber.

3. Amine-Curing Studies Utilizing the Ball Rebound Technique

Results from the ADL ball rebound test of the master batches helped to produce the best curing procedures. Rebound data of master batches 37593-1, 37593-2, 52905-1, 52911-1, 52911-2, 52912-1, and 52912-2, show that the rubbers go through three to four different stages as they are heated (see Figures 40, 41, 42). These stages produced the best temperature ranges for postcuring and also gave an indication of the highest temperature (critical temperature, at which the sample should be press cured. This critical temperature was about 230°F for the Thiokol XP5887 rubbers and about 215-220°F for the Thiokol XP5702 and PCR rubbers. The postcuring steps were taken from Figure 40. These temperatures correspond to positions of the stages on the rebound cures.

Figure 40 illustrates the effect of various types and amounts of filler in a particular amine gum system. All samples have similar rebound curves. They have a peak or a leveling-off between 115°F to 145°F, and all level-off between 145°F to 205°F. They also have a peak between 190°F to 230°F. These ranges vary in magnitude in each case, due primarily to the amount of filler and the hardness of the specimen due to cure. Sample 37953-2A, which should have been the hardest, due to the higher filler content, did not have this characteristic.

Figure 41 shows the effect of various types and quantities of amine. Their rebound curves are similar, showing peaks at 115°F, a peak or leveling-off between 145°F to 190°F, and a peak between 220°F and 230°F. Sample 52911-2A also had a peak at 140°F. Little difference was shown between the two samples except that 52911-2A exhibited a considerable rebound drop at 120°F which may have been due to some initial decomposition or degassing. The final product as shown by the hardness values of 43 and 45 (Table 9) was apparently little different.

The effect of the $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ copolymer is shown in Figure 42 for two different gums produced by Thiokol and Peninsular ChemResearch. Their rebound curves are similar, exhibiting a peak or leveling-off between 85°F to 120°F, a peak between 135°F to 160°F, a peak between 190°F

to 215°F, and a falling off or a peak between 220°F to 230+°F. Samples 52912-2A also had a peak between 175°F to 195°F. These ranges vary in magnitude in each case. Both of these samples "sponged" during the test, indicating that these samples may have had a lower critical temperature than the others. The erratic curing nature of sample 52912-1A (Thiokol) resulted in a poorly cured specimen, indicated by no change in hardness during cure (Table 9).

T. SOLVENT AND CHEMICAL RESISTANCE OF THE AMINE-CURED CF₃NO/C₂F₄ RUBBERS

The increase (and decrease) of weight and volume of the cured CF₃NO/C₂F₄ copolymer in 14 solvents and chemicals is shown in Table 10.

The densities of the solvents and chemicals indicate that the volume swell is not due merely to porosity of the rubber and subsequent pickup of the liquid.

Note that the rubber was swollen by all of the liquids, including water, indicating that it was poorly cross-linked. The FC-75, FC-43, and Freon 113 swelled the rubber significantly. Extractables were not indicated by a change in viscosity of the solvent; however, slight CF₃NO/C₂F₄ concentrations were observed in an IR analysis of the solution.

Volume swell analysis for four different rubbers in FC-75 is shown in Table 11. The rubbers are all amine-cured and consist of two samples prepared from XP5887, one from XP5702, and one from PCR-bulk-polymerized gum. In all cases, extreme swelling indicated a poorly cross-linked structure to the point of sample 52912-2-1 which fell apart in time.

As expected, those samples with the least amount of swell (52905-1-1) exhibited the best mechanical properties (see Table 8).

U. THERMOGRAVIMETRIC ANALYSIS OF THE AMINE-CURED
CF₃NO/C₂F₄ COPOLYMER

The violent thermal decomposition in air at 260°C, that had previously been demonstrated on the gum (Section I), was shown to occur with the rubber. Decomposition of the rubber in helium occurred over the temperature range from 150° through 320°C. Note that extreme caution should be used in handling this rubber at elevated temperatures (above 250°C).

V. CONCLUSIONS

The utility of three solvents, FC-75 (isomers of $C_8F_{16}O$), FC-43 [$(C_4F_9)_3N$], and Freon 113 ($CCl_2FCCl_2F_2$), for solution measurements on production lots of CF_3NO/C_2F_4 gums was demonstrated. FC-75 was shown to be the solvent with highest utility since solution occurred in the shortest time, the viscosity was relatively low, and the solvent could be removed readily by evaporation (bp $100^\circ C$). Even at its best, however, the FC-75 would not be considered to be an outstanding solvent. Intrinsic viscosities of only 1.7 were noted for the high molecular weight gums (3×10^6) and 0.4 for a molecular weight of $\sim 5 \times 10^5$.

The Huggins K' and K'' constants for CF_3NO/C_2F_4 (production) in FC-75 were determined to be 0.396 and 0.124, respectively. In general, the K' of the CF_3NO/C_2F_4 in FC-75 was greater than that in FC-43 or Freon 113, which indicates the improved solubility in the FC-75 solvent. All characterization of the Thiokol production CF_3NO/C_2F_4 gums, especially including solution studies, was complicated by the presence of a large amount of insolubles and a sizable low-molecular-weight volatile portion. The insoluble portion consisted of 25% to 50% gel and $\sim 3\%$ insoluble basic magnesium carbonate trihydrate. The low-molecular-weight portion amounted to 20% by weight of the polymer, having a molecular weight below 2×10^5 . This portion apparently was, however, only low-molecular-weight copolymer, as shown by NMR, elemental analysis, and mass spectrographic analysis.

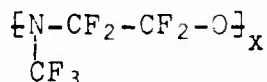
Various fingerprinting techniques were developed to allow rapid and simple determination of batch-to-batch similarity. The more precise technique consisted of measuring solution viscosities in two different solvents. This technique readily determined that differences existed in all batches submitted. It was shown that the precision provided was not required to show the major differences which existed. Instead a simpler technique utilizing Vicat indentation with temperature was shown to be just as useful and simpler. The Vicat technique utilizes a piece of gum as submitted; therefore, it requires no forming or causing solution. Vicat temperature differences as little as $0.2^\circ C$ were observable and significant.

Although the fingerprinting techniques were not set up to determine what differences existed, but only if they did exist, the varying amounts of low molecular weight gum were shown to be the prime contributing factor.

Elemental analysis confirmed the elemental nature of C_3F_7NO to within 4% of typicality, which improved with time to 0.15%. In all the Thiokol production gums observed, the typicality of the elemental analysis increased with time. The improvement in analysis may have been due to a volatilization of some atypical product in the low-molecular-weight portion and the selection of a better, however less representative, specimen. The only atypical product that was identified was the basic magnesium carbonate trihydrate. Based upon the good elemental analysis, the ability to improve elemental analysis by vacuum drying, and the quantity available, the Thiokol XP5702 gum was selected as the typical gum for characterization purposes.

Infrared analysis indicated C-F stretching, $-CF_2-CF_2-$ bend, and C-O-N stretching. Either $-CF_2-CF_2-$ or $-CF-CF-$ were indicated, even though they do not exist in the idealized average structure. Degradation was noted by some rearrangements to halogenated ketones and acids. No hydrogen was shown.

The structure was confirmed by nuclear magnetic resonance to be:

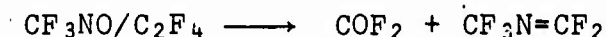


No further definition could be obtained due to poor solubility of the gum.

The gum was noncrystalline from -70° to $28^\circ C$.

The weight loss with temperature of the CF_3NO/C_2F_4 gum was shown to start at $\sim 75^\circ C$, then continue gradually to $260^\circ C$ where a rapid weight loss occurred (in larger quantities the rapid loss would have been considered explosive). Isothermal weight loss data indicated that a loss of up to 20% of the weight occurred before $150^\circ C$ with a peak loss $\sim 100^\circ C$; then, the remainder of the specimen was lost with a peak $\sim 250^\circ C$. Each temperature established

an equilibrium weight, indicating that each weight loss was associated with a particular molecular weight fraction; thus, the polymer had a bimodal distribution. This loss was identical in an inert gas as in air, indicating no effect of oxygen on thermal failure. Mass spectrographic analysis confirmed, but did not establish, the primary mode of decomposition to be



and differential thermal analysis confirmed the decomposition temperature of $\sim 260^\circ\text{C}$.

The density of the $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ gum was 1.937 ± 0.001 g/cc.

Elution fractionation of the $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ copolymer, utilizing a FC-75/benzotrifluoride solvent/nonsolvent system, was demonstrated as being highly successful. The success was demonstrated in just the third fractionation of this entirely new polymer solvent system. Utilizing 1% solvent increments, as many as 25 fractions were obtained with ease. The number and quantities of fractions obtained could readily be adjusted by selecting elution solvent increments and an elution temperature of 56.6°C was found to provide the most usable (in terms of quantity) selective elution. Approximately 1.5 g were fractionated per batch.

Fractionation of two of the Thiokol production $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ samples from which 25% gel had been removed indicated a bimodal distribution. The two molecular weight peaks were located at 5.7×10^6 and $\sim 2 \times 10^5$. The high molecular weight portion was not symmetrical about its peak, primarily, because of the weighting of the low-molecular-weight portion. This bimodal distribution was shown earlier in the thermogravimetric analysis, indicated by an identical temperature distribution curve.

Molecular weight determinations on the $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ copolymer by light-scattering were shown to be readily, although tediously, obtainable in the FC-75 solvent. Zimm data, due to the FC-75 apparently being close to a critical consolute solvent, were not usable. However H_c/τ P(90°) extrapolation to zero concentration provided reasonable molecular weight data. Molecular weights from 0.56×10^6 to 3.9×10^6 were determined with corresponding intrinsic viscosities of 0.42 and 1.69.

The Mark-Houwink equation was determined to be:

$$[\eta] = 3.2 \times 10^{-5} M_w^{0.72}$$

The a value of the FC-75 solvent indicated the improved solubility of the $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ copolymer in FC-75 over FC-43 and Freon 113, which were nearer the value of 0.5 for a Flory θ solvent, i.e., $0.72 > 0.66 > 0.51$.

Utilizing the Mark-Houwink equation, the determined constants in FC-75, and the viscosities in FC-75, the M_w , M_n , and M_w/M_n , for the Thiokol XP5702 samples were determined to be:

	M_w	M_n	M_w/M_n
Run 3	3.4×10^6	2.7×10^4	125
Run 4	3.4×10^6	1.9×10^5	18

The low values and considerable differences in M_n , and accordingly high M_w/M_n values, were due primarily to the presence of the sizable low-molecular-weight portion of $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ gum. These values, however, were characteristic of the production $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ gums.

The glass transition temperature (T_g) of the $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ gums was determined by a number of techniques. By low temperature differential thermal analysis, the T_g was shown to be in the region of -41° to -46°C with the various samples being within 2°C of each other. By linear coefficient of expansion, the T_g was shown to be from -46° to -49°C . The most typical production gums exhibited the lower T_g 's, down to -49°C , probably due to the presence of the low-molecular-weight portion which acted as a plasticizer. The purified gums exhibited a characteristic T_g of $-47 \pm 2^\circ\text{C}$.

The $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ copolymer gum is readily degraded by refluxing amines with losses in molecular weights of two orders of magnitude, i.e., from 10^6 to 10^4 .

Amine-curing of the SiO_2 -filled $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ production gums, utilizing the 3M-determined formulation and cure cycle (standard cure cycle), was unsuccessful in terms of producing the mechanical properties reported by 3M and the U.S. Army Natick Laboratories. Modification of the standard cure cycle to longer times and lower temperatures followed by extended stepped post cures resulted in the best rubber, having a 267 psi tensile strength, 420% elongation, and hardness of 47 (Shore A).

The glass transition temperature of the modified cure standard rubber was -49°C (Clash-Berg technique) with a Stifflex range of 16.5°C . The 3 cps and 1000 cps temperatures of maximum loss modulus were $-42 \pm 2^\circ\text{C}$ and $-10 \pm 2^\circ\text{C}$, respectively. These modulus measurements indicated the utility of the $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ rubber at low temperatures. Reasonable flexibility is available as low as -55°C , and the rubber may well be utilized much below -70°C .

The utility of MgO filler as a scavenger to prevent blistering and thus produce a higher strength rubber was demonstrated. Strengths of 350 psi tensile over 270 psi and elongations of 540% over 420% were obtained. Room temperature cures and low reactive amine (FC-43) cures were unsuccessful. The addition of a small amount of carbon black, 0.01%, was shown to increase mechanical properties by 5%. The mechanical properties of carbon-black-reinforced rubbers were not consistent. A tensile strength of 290 psi and 423% elongation was obtained, which indicates that carbon black should not be eliminated from consideration as a filler.

The best mechanical properties obtained were the result of the utilization of a Peninsular ChemResearch-bulk-polymerized gum in a SiO_2/MgO -filled system. The tensile properties were 387 psi strength and 527% elongation. These results strongly indicate that the quality or nature of the gum is a most significant factor in obtaining good mechanical properties. The only significant differences between the PCR and Thiokol gums, however, were the high insoluble content of the Thiokol gums and the lower molecular weight of the PCR gums. It might be concluded that the Thiokol gums were hindered from cross-linking due to their extremely high molecular weight (20% greater than 6×10^6). The reason that the PCR rubbers did not exhibit the 3M and U.S. Army Natick Laboratories' reported physical properties was not determined.

Curing studies on the amine $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ system indicated that there were significant temperature plateaus of degradation and cross-linking. Curing of the rubber at temperatures above these plateaus resulted in poor properties. It was concluded that press cures should be conducted at temperatures below the first plateau ($\sim 150^\circ\text{F}$) in order to obtain a suitable packing and surface, followed by oven postcures at temperatures below the final plateau. The oven postcures should be conducted stepwise from below the first plateau temperature to the final plateau temperature.

Metal-to-metal adhesive shear strength was shown to be 180 psi and of a cohesive nature. The rubber-to-metal strength would probably be well above 180 psi for a good rubber.

The solvent and chemical resistance of the amine-cured rubbers was shown to be extremely poor, probably because they were poorly cross-linked. While it was not conclusively shown, it would be expected that the $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ rubber would potentially exhibit excellent solvent and chemical resistance, because the rubbers were not soluble in any of the solvents or chemicals examined.

The thermal stability of the $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ rubber was shown to be identical to the gum, exhibiting violent decomposition at $\sim 260^\circ\text{C}$. No thermal stability was added to the gum by cross-linking.

The bulk-polymerized Peninsular ChemResearch $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ copolymer was similar to the Thiokol gums in terms of all properties except purity and molecular weight. Significantly, the PCR gum had a sizable insoluble gel portion and a bimodal molecular weight distribution of the Thiokol gums. No basic magnesium carbonate dihydrate was seen, however. The M_w , M_n , and M_w/M_n of the PCR gum were:

$$\begin{aligned}M_w &= 2 \times 10^6 \\M_n &= 2.3 \times 10^4 \\M_w/M_n &= 88\end{aligned}$$

Again the M_n and M_w/M_n were strongly influenced by the sizable low-molecular-weight portion. The average molecular weight was 1.4×10^6 less than the Thiokol gum. As discussed above, the mechanical properties of the PCR rubber were significantly better than the rubber produced from the Thiokol gums.

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APPENDIX A.

TABLES

Table 1

ELEMENTAL ANALYSIS AND "ATYPICALITY" OF $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ GUMS

Sample No.	C		H		N		P		O ^a		Atypicality, $\frac{D}{\Delta \text{Wt. } \pm}$	
	12/10/64	3/6/65	12/10/64	3/6/65	12/10/64	3/6/65	12/10/64	3/6/65	12/10/64	3/6/65	12/10/64	3/6/65
CF_3NO	18.10	-----	0.00	-----	7.04	-----	66.82	-----	8.04	-----	0.00	-----
XP5675	18.29	18.52 ^c	0.15	0.00 ^c	6.27	6.75 ^c	61.51	58.54 ^c	13.79	16.19 ^c	3.94	5.82 ^c
XP5702	18.29	18.31	0.12	0.10	6.26	6.92	66.06	66.65	9.31	6.02	0.84	0.31
XP5512	18.54	-----	0.09	-----	6.30	-----	66.61	-----	3.46	-----	0.49	-----
XP5587	18.54	-----	0.06	-----	6.38	-----	67.34	-----	7.68	-----	0.51	-----
PCR-Sulk	-----	18.24	-----	0.16	-----	-----	66.67	-----	-----	-----	-----	0.14
PCR-Solution	-----	19.20	-----	0.13	-----	6.90	66.79	-----	-----	7.98	-----	0.11

^a Oxygen by difference.

^b $\left(\frac{\sum (X-X)^2}{n-1} \right)^{1/2}$, where X = analysis, \bar{X} = theory, n = no. of elements reported.

^c Vacuum dried XP5702.

Table 2

SOLUBILITIES OF $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ IN FC-75 AND BENZOTRIFLUORIDE

Temperature, °C	*Solution: Benzotrifluoride ml:ml	Condition of Solution, Visual
23	100:91.2	Polymer all out
80	100:91.2	Polymer all in
58	100:91.2	Hazy
43	100:91.2	Definite fraction drop out
40	100:91.2	Polymer all out

*Solution = XP5702/FC-75 = (2.0 g/100 ml)

Table 3

**ELUTION FRACTIONATION OF CF₃NO/C₂F₄ GUM XP5702
FOLLOWING SELECTIVE DEPOSITION - RUN NO. 3**

Solvent Mixture ⁷		Bromo- trifluoride		Weight of Fraction g	Polymer eluted g	Cumulative Polymer eluted g	η_{sp}^2	η_{sp}/C^2	η_{sp}/C^2	$[\eta]^6$	$[\eta]^5$	$[\eta]^4$	$[\eta]^3$	$[\eta]^2$	$[\eta]$	$M \times 10^{-3}$
Fraction	ml	ml	g													
Plush	0	200	0.0811	5.84	5.84	5.84	0.001	0.01	---	---	0.010	---	---	2.92	0.03	---
1	35	65	0.1426	10.27	16.11	16.11	0.001	0.01	---	---	0.010	---	---	10.97	0.03	---
2	36	64	0.0107	0.77	16.88	16.88	0.011	0.11	---	---	0.110	---	---	16.49	0.87	---
3	37	63	0.0036	0.26	17.14	17.14	---	---	---	---	---	---	---	17.01	---	---
4	38	62	0.0051	0.37	17.51	17.51	---	---	---	---	---	---	---	17.32	---	---
5	39	61	0.0036	0.26	17.77	17.77	---	---	---	---	---	---	---	17.63	---	---
6	40	60	0.0025	0.18	17.95	17.95	---	---	---	---	---	---	---	17.85	---	---
7	41	59	0.0038	0.27	18.22	18.22	---	---	---	---	---	---	---	18.08	---	---
8	42	58	0.0123	0.89	19.11	19.11	0.016	0.16	---	---	0.160	---	---	18.66	1.46	---
9	43	57	0.0128	0.99	20.10	20.10	0.025	0.25	---	---	0.250	---	---	19.60	2.72	---
10	44	56	0.0209	1.50	21.60	21.60	0.033	0.33	0.037	---	0.326	---	---	20.85	3.94	---
11	45	55	0.0242	1.74	23.34	23.34	0.049	0.49	---	---	0.481	---	---	22.17	6.78	---
12	46	54	0.0401	2.89	26.23	26.23	0.060	0.60	---	---	0.586	---	---	24.75	8.93	---
13	47	53	0.0787	5.67	31.90	31.90	0.087	0.87	0.088	---	0.842	---	---	29.36	14.80	---
14	48	52	0.1821	13.11	45.01	45.01	0.129	1.29	---	---	1.230	---	---	38.45	25.11	---
15	49	51	0.3212	23.12	68.13	68.13	0.180	1.80	---	---	1.687	---	---	56.57	39.01	---
16A	50	50	0.2693	19.39	87.52	87.52	0.224	2.24	---	---	2.071	---	---	77.83	51.93	---
17A	Column Dried		0.0891	6.41	93.93	93.93	0.237	2.37	0.233	---	2.183	---	---	50.73	55.89	---
16B	50	50	0.0052	0.37	94.30	94.30	0.126	1.26	---	---	---	---	---	94.12	---	---
17B	51	49	0.0317	2.28	96.58	96.58	0.083	0.83	---	---	---	---	---	95.45	---	---
18	52	48	0.0151	1.09	97.67	97.67	0.102	1.02	---	---	---	---	---	97.13	---	---
19	53	47	0.0047	0.34	98.01	98.01	---	---	---	---	---	---	---	97.85	---	---
20	54	46	0.0047	0.34	98.35	98.35	---	---	---	---	---	---	---	98.19	---	---
21	55	45	0.0079	0.57	98.92	98.92	0.258	2.58	---	---	2.359	---	---	98.64	62.27	---
22	100	0	0.0023	0.17	99.09	99.09	---	---	---	---	---	---	---	99.01	---	---
23	100	0	0.0031	0.22	99.31	99.31	---	---	---	---	---	---	---	99.20	---	---
24	200*	0	0.0096	0.69	100.00	100.00	---	---	---	---	---	---	---	99.65	---	---
Unrecovered	-	-	0.1110	0.69	---	---	---	---	---	---	---	---	---	---	---	---
Total			1.5000	100.00	---	---	---	---	---	---	---	---	---	---	---	---
Whole polymer, cleaned up							0.139	1.39	1.418	1.193	1.418	1.193	---	---	---	---
Whole polymer as received							0.114	1.14	---	---	---	---	---	---	---	---

- 1 based on recovered amount of 1.3890
- 2 0.1% solution in PC-75 at 25°C
- 3 insufficient to recover or measure
- 4 0.1% solution in PC-75 at 35°C
- 5 in PC-75 at 25°C
- 6 in PC-43 at 25°C
- 7 Eluted at 56.5°C
- 8 Eluted at 78.5°C
- 9 1.5% A₂
- 10 Molecular weight of 1st fraction
- 11 <0.1% solution in PC-75 at 25°C

Table 4

ELUTION FRACTIONATION OF $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ GUM XP5702
FOLLOWING SELECTIVE DEPOSITION - RUN NO. 4

Fraction	Solvent Mixture ⁷		Weight of Fraction, g	Polymer ¹ Eluted, %	Cumulative ¹ Polymer Eluted, %	η_{sp} ²	η_{sp}/C ²	[η] ⁵	$\bar{M}_n + 1/2 \Delta$, ⁹ %	$\bar{M}_n \times 10^{-5}$ ¹⁰
	FC-75, ml	Benzo- trifluoride, ml								
Flush	0	200	.0984	8.29	8.29	.004	.04	.040	4.14	0.21
1	35	65	.1169	9.85	18.14	.006	.06	.060	13.21	0.37
2	38	62	.0160	1.35	19.49	.013	.13	.130	18.81	1.09
3	41	59	.0069	.58	20.07	.2911	.29	.290	19.77	3.35
4	42	58	.0165	1.39	21.46	.031	.31	.310	20.76	3.67
5	43	57	.0002	.02	21.48	-----3	-----	-----	21.46	-----
6	44	56	.0220	1.85	23.33	.041	.41	.404	22.39	5.32
7	45	55	.0262	2.21	25.54	.061	.61	.596	24.42	9.15
8	46	54	.0432	3.64	29.18	.064	.64	.625	27.35	9.77
9	47	53	.0879	7.40	36.58	.088	.88	.851	32.87	15.0
10	48	52	.1614	13.59	50.17	.126	1.26	1.203	43.36	24.4
11	49	51	.3488	29.38	79.55	.190	1.90	1.775	64.85	41.9
12	50	50	.1444	12.16	91.71	.252	2.52	2.309	85.62	60.5
13	51	49	.0421	3.55	95.26	-----3	-----	-----	93.47	-----
14	55	45	.0177	1.49	96.75	-----3	-----	-----	95.99	-----
15	.60	40	.0135	1.14	97.89	-----3	-----	-----	97.31	-----
16	100	0	.0048	.40	98.29	-----3	-----	-----	98.07	-----
17	100	0	.0205	1.73	100.02	-----3	-----	-----	99.14	-----
Unrecovered			.3126	-----	-----	-----	-----	-----	-----	-----
Total			1.5000	100.02						

¹ Based on recovered amount of 1.1874.² 0.1% solution in FC-75 at 25°C.³ Insufficient to recover or measure.⁴ 0.1% solution in FC-75 at 25°C.⁵ In FC-75 at 25°C.⁶ In FC-43 at 25°C.⁷ Eluted at 56.5°C.⁸ Eluted at 78.5°C.⁹ $\bar{M}_n + 1/2 \Delta$, %.¹⁰ Molecular weight of 11th fraction.¹¹ <0.1% solution in FC-75 at 25°C.

Table 5

ELUTION FRACTIONATION OF PCR-BULK-POLYMERIZED $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$
COPOLYMER FOLLOWING SELECTIVE DEPOSITION

Fraction	Solvent Mixture ⁷ FC-75, ml	Benzo- trifluoride, ml	Weight of Fraction, g	Polymer ¹ Eluted, %	Cumulative ¹ Polymer Eluted, %	η_{sp}^2	η_{sp}/c^2	$[\eta]^5$	$I + 1/2 \Delta$, ⁹ %	$M_n \times 10^{5.10}$
Flush	0	200	.2741	21.26	21.26	.001	.01	.010	10.63	0.03
1	25	65	.1593	12.36	33.62	.004	.04	.046	27.44	0.21
2	38	62	.0126	.98	34.60	.012	.11	.110	34.10	0.87
3	41	59	.0074	.57	35.17	.200 ¹¹	.26	.200	34.88	1.99
4	42	58	.0120	.93	36.10	.029	.29	.290	35.63	3.35
5	43	57	.0192	1.49	37.59	.040	.40	.394	36.84	5.14
6	44	56	.0145	1.12	38.71	.045	.45	.442	38.15	6.03
7	45	55	.0233	1.81	40.52	.044	.44	.433	39.62	5.86
8	46	54	.0525	4.07	44.59	.058	.58	.567	42.56	8.53
9	47	53	.0800	6.20	50.79	.077	.77	.747	47.69	12.5
10	48	52	.1766	13.70	64.49	.113	1.13	1.083	57.64	21.0
11	49	51	.2203	17.09	81.58	.156	1.56	1.473	73.04	32.3
12	50	50	.1836	14.24	95.82	.195	1.95	1.819	88.70	43.3
13	51	49	.0324	1.74	97.56	1.95 ¹¹	1.95	1.919	96.69	46.7
14	55	45	.0102	.79	98.35	----- ³	-----	-----	97.95	-----
15	60	40	.0059	.46	98.81	----- ³	-----	-----	98.59	-----
16	100	0	.0061	.47	99.28	----- ³	-----	-----	99.05	-----
17	100	0	.0093	.72	100.00	----- ³	-----	-----	99.50	-----
Unrecovered			.2107	-----	-----	-----	-----	-----	-----	-----
Total			1.5000	100.00						

¹ Based on recovered amount, 1.2893.

² 0.1% solution in FC-75 at 25°C.

³ Insufficient to recover or measure.

⁴ 0.1% solution in FC-75 at 35°C.

⁵ In FC-75 at 25°C.

⁶ In FC-43 at 25°C.

⁷ Eluted at 56.5°C.

⁸ Eluted at 78.5°C.

⁹ $I + 1/2 \Delta$, %

¹⁰ Molecular weight of i'th fraction.

¹¹ 0.1% solution in FC-75 at 25°C.

Table 6

"APPARENT" LINEAR THERMAL EXPANSION COEFFICIENTS

OF CF₃NO/C₂F₄ GUMS

Sample No.	"Apparent" Linear Expansion Coefficient, ^a °C ⁻¹	Temperature Range, °C	Tg, ^b °C
XP5675 ^c	7.2 x 10 ⁻⁵	-67 to -52	-46
	1.2 x 10 ⁻⁴	-52 to Tg	
XP5702	8.2 x 10 ⁻⁵	-67 to -52	-46
	1.2 x 10 ⁻⁴	-52 to Tg	
XP5812	7.6 x 10 ⁻⁵	-72 to Tg	-49
XP5887	5.7 x 10 ⁻⁵	-72 to -62	-48
	8.8 x 10 ⁻⁵	-62 to Tg	

^a "Apparent" due to temperature rate rise of about 1°C/min (see test).

^b From thermal expansion data.

^c Devolatilized 16 hours at 80°C and 3 mm Hg.

Table 7

MOLECULAR WEIGHT DEGRADATION OF CF_3NO/C_2F_4 BY AMINES

	Original			Refluxed 1 Hour ¹			Refluxed 67 Hours ²		
	Specific Viscosity	Intrinsic Viscosity	Mw x10 ⁶	Specific Viscosity	Intrinsic Viscosity	Mw x10 ⁶	Specific Viscosity	Intrinsic Viscosity	Mw x10 ⁶
Low Mw ³	0.066	0.644	1.0	0.009	0.09	0.07	-----	-----	--
Med Mw ⁴	0.147	1.39	2.3	0.016	0.16	0.12	0.012	0.12	0.08
High Mw ⁵	0.252	2.31	6.0	0.01	0.10	0.08	-----	-----	--

1 refluxed with cyclohexylamine

2 refluxed with n-butyl amine

3 XP5675

4 XP5702

5 XP5702 fraction

Table 8

**COMPOUNDING RECIPES AND MECHANICAL TEST RESULTS
OF AMINE-CURED CF₃NO/C₂F₄ RUBBERS**

Ingredient Parts by Weight	Compound Numbers											
	37559 Cure #1	37559 Cure #2	37559 Cure #3	37559 Cure #4	37559 Cure #5	37559 Cure #6	37559 Cure #7	37559 Cure #8	37566 Cure #1	37566 Cure #2	37566 Cure #3	
Nitroso, Thiokol XP-5812 (Purified) 100	100	100	100	100	100	100	100	100	100	100	100	
Nitroso, Thiokol XP-5887												
Nitroso, Thiokol 5702 (Purified)												
Nitroso, Peninsular Chem. Research (Purified)												
HiSil 101	15	15	15	15	15	15	15	15	15	15	15	
MGO (Maglite D)												
Triethylenetetramine (TETA)	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	
Hexamethylenediamine	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	
Carbamate (HMDAC)												
PC-43												
Carbon Blacks												
Viton L M												
Oxydianiline												
Press Cure, Time min./Temp °F	50/250	50/250	50/250	50/250	50/250	300/250	300/250	300/250	120/250	120/250	150/250	
Oven Cure, Time hours/Temp °F	18/120	18/120	18/120	1/120	1/150	18/30-	18/30-	18/30-	16/122	16/122	16/122	
				1/150	1/185	212	212	212	2/158	2/158	2/158	
				1/185	18/212				2/194	2/194	2/194	
				18/212					16/203	16/203	16/203	
Tensile Strength, psi	130			210	232			267			110	
Ultimate Elongation, %	100			400	420			420			185	
Stress at 300% Elong. psi												
Stress at 100% Elong. psi												
Hardness, Shore A-2	27			38	39			47				

Carbon Blacks:

- 1 Thermax M
- 2 Sterling S
- 3 Elastocar

Table 8 (Cont'd)

Ingredients Parts by Weight	37566 Cure #4	37566 Cure #5	37566 Cure #6	37568 Cure #1	37568 Cure #2	Compound Numbers 37568 Cure #3	37568 Cure #4	37572 Cure #1	37572 Cure #2	37572 Cure #3
Nitroso, Thiokol XP-5812 (Purified)	100	100	100	100	100	100	100	100	100	100
Nitroso, Thiokol XP-5887										
Nitroso, Thiokol 5702 (Purified)										
Nitroso, Peninsular Chem. Research (Purified)										
HiSil 101	15	15	15	15	15	15	15	15	15	15
MgO (Maglite D)										
Triethylenetetramine (TETA)	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25
Hexamethylenediamine Carbamate (HMDAC)	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
PC-43										
Carbon Black #	1 ²	1 ²	1 ²	~0.25 ²	~0.25 ²	~0.25 ²	~0.25 ²			
Viton L M										
Oxydianiline										
Press Cure, Time min./Temp °F	210/266	210/266	210/266	210/266	180/266	210/266	300/246	210/248	210/266	300/248
Oven Cure, Time hours/Temp °F	50/122 3/158 20/176 4/194 4/203	20/122 4/158 4/176 16/194 8/203	16/122 5/158 3/176 16/194 6/203	20/122 4/158 4/176 16/194 8/203	21/122 5/158 3/176 16/194 6/203	16/122 5/158 3/176 16/194 6/203	1/122 1/149 1/185 18/212	17/122 3/158 5/185 17/203 5/212	17/122 3/158 5/185 17/203 5/212	4/122 10/167 3/185 5/203
Tensile Strength, psi:	--	--	79	78	76	98	118	208	124	--
Ultimate Elongation, %	--	--	155	115	140	173	177	315	285	--
Stress at 300% Elong, psi	--	--	--	--	--	--	--	--	--	--
Stress at 100% Elong, psi	--	--	--	--	--	--	--	--	--	--
Hardness, Shore A-2	--	--	--	--	--	--	--	--	--	78

*Carbon Blacks:

- 1 Thermax MT
- 2 Sterling S
- 3 Elastopar

Table 8 (Cont'd)

Ingredient Parts by Weight	Compound Numbers											
	37593-1 Cure #1	37593-1 Cure #2	37593-1 Cure #3	37593-1 Cure #4	37593-1 Cure #5	37593-1 Cure #6	37593-2 Cure #1	37593-2 Cure #2	37593-2 Cure #3	37593-2 Cure #4	37593-2 Cure #5	37593-3 Cure #1
Nitroso, Thiokol XP-5812 (Purified)	100	100	100	100	100	100	100	100	100	100	100	100
Nitroso, Thiokol XP-5887												
Nitroso, Thiokol 5702 (Purified)												
Nitroso, Peninsular Chem. Research (Purified)												
KiSil 101	15	15	15	15	15	15	15	15	15	15	15	50
MgO (Maglite D)	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25
Triethylenetetramine (TETA)												
Hexamethylenediamine												
Carbamate (HMDAC)	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
PC-43												
Carbon blacks*												
Viton L M												
Oxydianiline												
Press Cure, Time min./Temp °F	150/248	60/212	60/212	60/212	60/131	15/131 15/167 30/212	60/212	60/212	60/212	60/131	15/131 15/167 30/212	60/212
Oven Cure, Time hours/Temp °F	16/122 2/158 1/203 5/212	1/122 1/158 1/203 16/230	1/122 1/158 1/203 16/230	1/122 1/158 1/203 16/230	1/122 1/158 1/203 16/230	1/122 1/158 1/203 16/230	1/122 1/158 1/203 16/230	1/122 1/158 1/203 16/230	1/122 1/158 1/203 16/230	1/122 1/158 1/203 16/230	1/122 1/158 1/203 16/230	1/122 1/158 1/203 16/230
Tensile Strength, psi	186	227	227	270	273	284	314	313	337	370	338	370
Ultimate Elongation, %	370	443	443	492	430	483	277	243	275	200	282	200
Stress at 300% Elong, psi	170	189	189	210	225	222	---	---	---	---	---	---
Stress at 100% Elong, psi	83	97	97	109	110	110	193	211	227	257	295	257
Hardness, Shore A-2	49	50	50	48	44	42	64	65	63	64	64	64

*Carbon Blacks:

- 1 Thermax MT
- 2 Sterling S
- 3 Elastopar

Table 8 (Cont'd)

Ingredient Parts by Weight	Compound Numbers													
	37593-3 Cure #2	37593-3 Cure #3	37593-4 Cure #1	37593-4 Cure #2	37593-4 Cure #3	37593-5 Cure #1	37593-5 Cure #2	52905-1 Cure #1	52905-2 Cure #1	52911-1 Cure #1	52911-2 Cure #1	52912-1 Cure #1	52912-2 Cure #1	
Nitroso, Thiokol XP-5812 (Purified)	100	100	100	100	100	100	100	100	100	100	100	100	100	
Nitroso, Thiokol XP-5887	100	100	100	100	100	100	100	100	100	100	100	100	100	
Nitroso, Thiokol 5702 (Purified)	100	100	100	100	100	100	100	100	100	100	100	100	100	
Nitroso, Peninsular Chem. Research (Purified)	100	100	100	100	100	100	100	100	100	100	100	100	100	
Hs11 101	50	50	15	15	15	15	15	7.5	7.5	7.5	7.5	7.5	7.5	
MgO (Maglite D)	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	
Tetrabutyltetramine (TETA)	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	
Hexamethylenediamine	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	
PC-45 Carbamate (HMDAC)	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	
PC-45 Blacks*	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	
Viton L M	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	
Oxydianiline	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	
Press Cure, Time min./Temp °p	60/212	60/212	60/212	60/212	60/212	60/212	60/212	60/212	60/212	60/131	60/131	15/131 15/167 30/212	15/131 15/167 30/212	
Oven Cure, Time hours/Temp °p	1/122 1/167 1/185 1/203 16/212 1/230 1/239 2/257	16/122 1/158 1/176 1/185 1/203 1/212 1/230 2/257	16/122 1/167 1/212 16/230 2 1/2/257	1/122 1/167 1/212 16/230 2/257	1/122 1/167 1/185 1/203 16/212 1/230 2/239	1/122 1/167 1/185 1/203 16/212 1/230 2/239	1/122 1/167 1/185 1/203 16/212 1/230 2/239	16/122 1/158 1/176 17/212 17/230 1/239 2/257	16/122 1/158 1/176 17/212 17/230 1/239 2/257	16/122 1/158 1/176 16/212 16/230 1/239 2/257	16/122 1/158 1/176 16/212 16/230 1/239 2/257	16/122 1/158 1/176 16/212 16/230 1/239 2/257	16/122 1/158 1/176 16/212 16/230 1/239 2/257	
Tensile Strength, psi	Cracked after press	Cracked after press	41	56	51	53	53	312	290	250	215	387	171	
Ultimate Elongation, %	after press	after press	50	70	100	80	80	540	473	295	353	527	427	
Stress at 300% Elong, psi	press	press	--	--	--	--	--	221	221	--	208	231	135	
Stress at 100% Elong, psi	at	at	--	--	--	--	--	107	103	125	102	90	70	
Hardness, Shore A-2	90	90	41	42	45	42	42	145	146	144	36	42	34	

*Carbon Blacks:

- 1 Thermax MT
- 2 Sterling S
- 3 Elastopar

Table 9

CF₃NO/C₂F₄ RUBBER HARDNESS VALUES PRIOR TO AND
AFTER CURING IN THE BALL REBOUND APPARATUS

<u>Sample No.</u>	<u>Durometer Before</u>	<u>Durometer After</u>	<u>Comments</u>
37593-1A	38	48	--
37593-2A	47	53	--
52905-1A	43	50	Sponged
52911-1A	39	45	Turned Brown
52911-2A	38	43	--
52912-1A	47	49	Sponged
52912-2A	32	32	Sponged

Table 10

**SOLVENT AND CHEMICAL RESISTANCE OF AN AMINE-CURED
CF₃NO/C₂F₄ RUBBER #37566 - CURE #1**

Immersion Fluid	Solvent Density	Specimen Volume (% Change from Initial)				Specimen Density (g/cc)				Specimen Wt. (% Change from Initial)			
		24 hr.	144 hr.	295 hr.	1128 hr.	Initial	24 hr.	144 hr.	295 hr.	Initial	24 hr.	144 hr.	295 hr.
FC-75	1.77	+240.0	+324.0	+335.0	+337.5	1.8397	1.8684	1.7125	1.7101	1.6990	1.6634	1.6634	1.6634
PC-43	1.32	+246.0	+272.0	+285.4	+302.1	1.8700	1.8890	1.9016	1.8877	1.8627	1.8783	1.8783	1.8783
Freon 113	1.45	+53.9	+59.3	+82.3	+70.2	1.8466	1.8439	1.8561	1.8518	1.8739	1.8646	1.8646	1.8646
Nitric Acid	1.502				+38.5	1.8630				1.7162	1.7535	1.7535	1.7535
Water	1.0				+18.4	1.9381				1.6974	1.7108	1.7108	1.7108
D.M.S.O.					+9.0	1.8896				1.8191	1.8090	1.8090	1.8090
Chromic/Sulfuric					+6.1	1.6528				1.8669	1.8719	1.8719	1.8719
Methyl Chloride	1.4237				+2.2	1.8514				1.8827	1.8858	1.8858	1.8858
Benzene	.87901	3.2			+1.4	1.8479	1.8171			1.9087	1.7920	1.7920	1.7920
M.E.K.	.808				+4.5	1.9614				1.8105	1.8045	1.8045	1.8045
Carbon Tetrachloride	.988				+4.7	1.8478				1.8585	1.8535	1.8535	1.8535
Acetone	.792				+2.7	1.8364				1.9167	1.8390	1.8390	1.8390
Freon 112		+2.7	+2.0	-2.7	+0.60	1.8362	1.8151	1.8172	1.8581	1.8681	1.8566	1.8566	1.8566
Ether					-3.7	1.8477				1.8853	1.8365	1.8365	1.8365
CF ₃ NO/C ₂ F ₄ #37559-B													
FC-75	1.77	362.0	411.4	(456 hr.)	(1412 hr.)	1.907	1.532	1.546	(456 hr.)	(1412 hr.)	271.3	315.1	307.4

Table 11

SWELL OF CF₃NO/C₂F₄ RUBBERS IN FC-75

Hours	XP5887 Gum 52905-1-1		XP5887 Gum 52911-2-1		PCR Gum 52912-1-1		XP5702 Gum 52912-2-1	
	% Wt Change	% Vol Change	% Wt Change	% Vol Change	% Wt Change	% Vol Change	% Wt Change	% Vol Change
24	264	282	316	342	252	272	449	498
48	269	298	323	359	256	294	456	513
72	274	306	326	364	261	295	469	546
216	299	330	343	386	284	328	469	517
240	304	349	342	388	285	328	Sample Broke	
312	319	358	349	394	300	349	---	---
1200	330	353	366	411	329	366	---	---

Table 12

NMR SPECTROGRAPHIC DATA AND ASSIGNMENTS
FOR CF₃NO/C₂F₄ GUM

Sample Number	Chemical Shift of ^b Peaks, ppm			Area Ratio of Peaks		
	1	2	3	1	2	3
XP5675	-11.4	+11.5	+24.0	3.0	1.9	2.0
XP5702	-11.4	+11.7	+24.2	3.0	2.0	1.9
XP5812	-11.3	+11.7	+24.3	3.0	1.9	2.0
XP5887	-11.5	+11.5	+24.0	3.0	2.0	1.9
Assignments				-N(CF ₃)	-N(CF ₂)CF ₂	-O(CF ₂)CF ₂

a F19 resonance at 40.0 Mc

b Reference trifluoroacetic acid

Table 13
MASS SPECTROGRAPHIC MASS ASSIGNMENTS
FOR THE CF₃NO/C₂F₄ COPOLYMER

<u>Mass</u>	<u>Possible Species</u>
30	NO
31	CF
47	CF=O
50	CF ₂
66	CF ₂ =O
69	CF ₃
99	CF ₃ NO
100	C ₂ F ₄
114	C ₂ F ₄ N
119	C ₂ F ₅
130	(CF ₂) ₂ NO
133	CF ₂ =N CF ₃
164	(CF ₂) ₂ NCF ₂ (or C ₆ F ₄ O)
180	-CF ₂ -N-O-CF ₂ CF ₃
199	-CF ₂ -N-O-CF ₂ CF ₃

APPENDIX B.

FIGURES

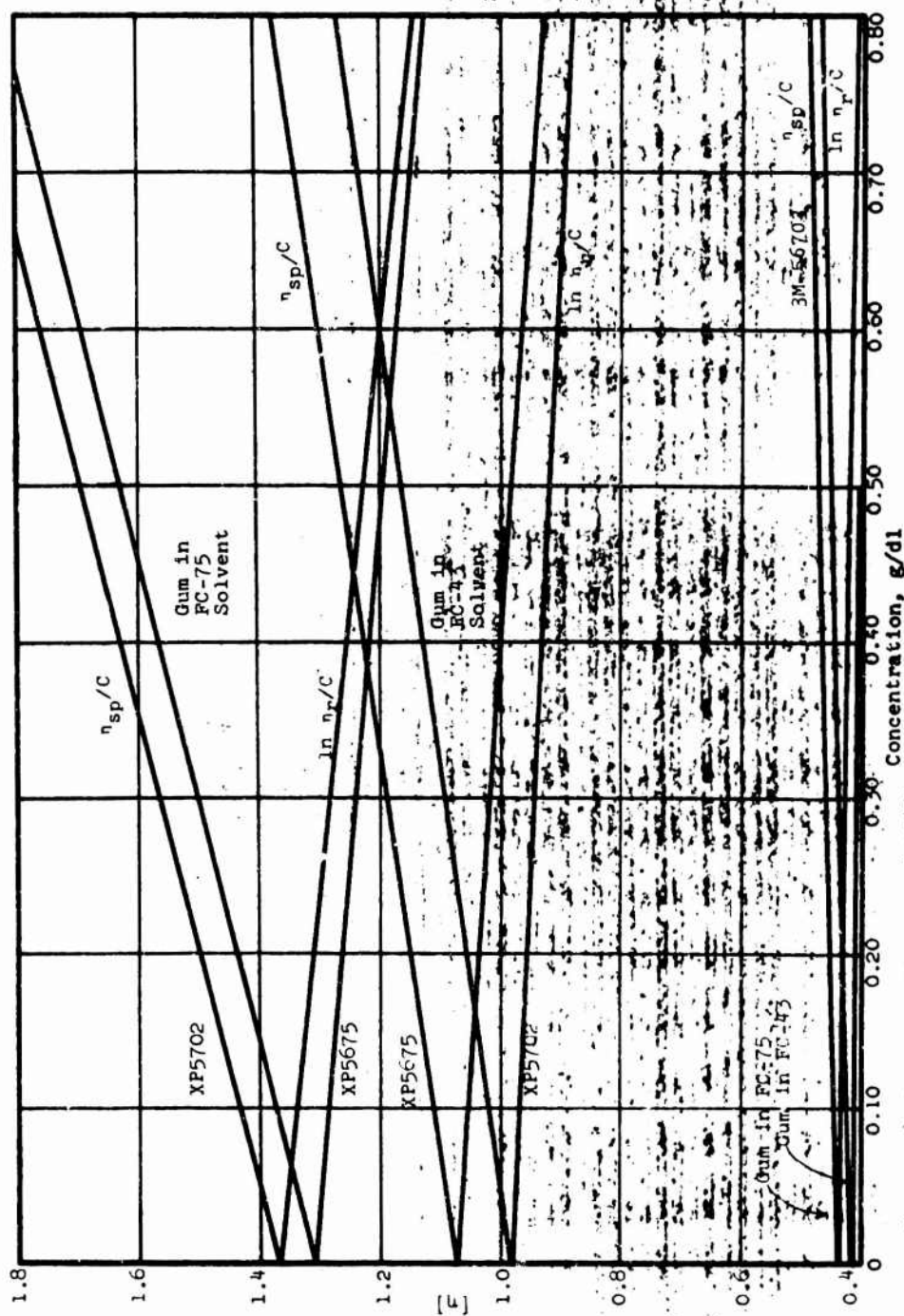


Figure 1. Reduced and Inherent Viscosities of XP5702, XP5675, and 3M-56703 $\text{CF}_3\text{NO/C}_2\text{F}_4$ Copolymers in FC-75 and FC-43 Fluorocarbon Solvents at 25°C.

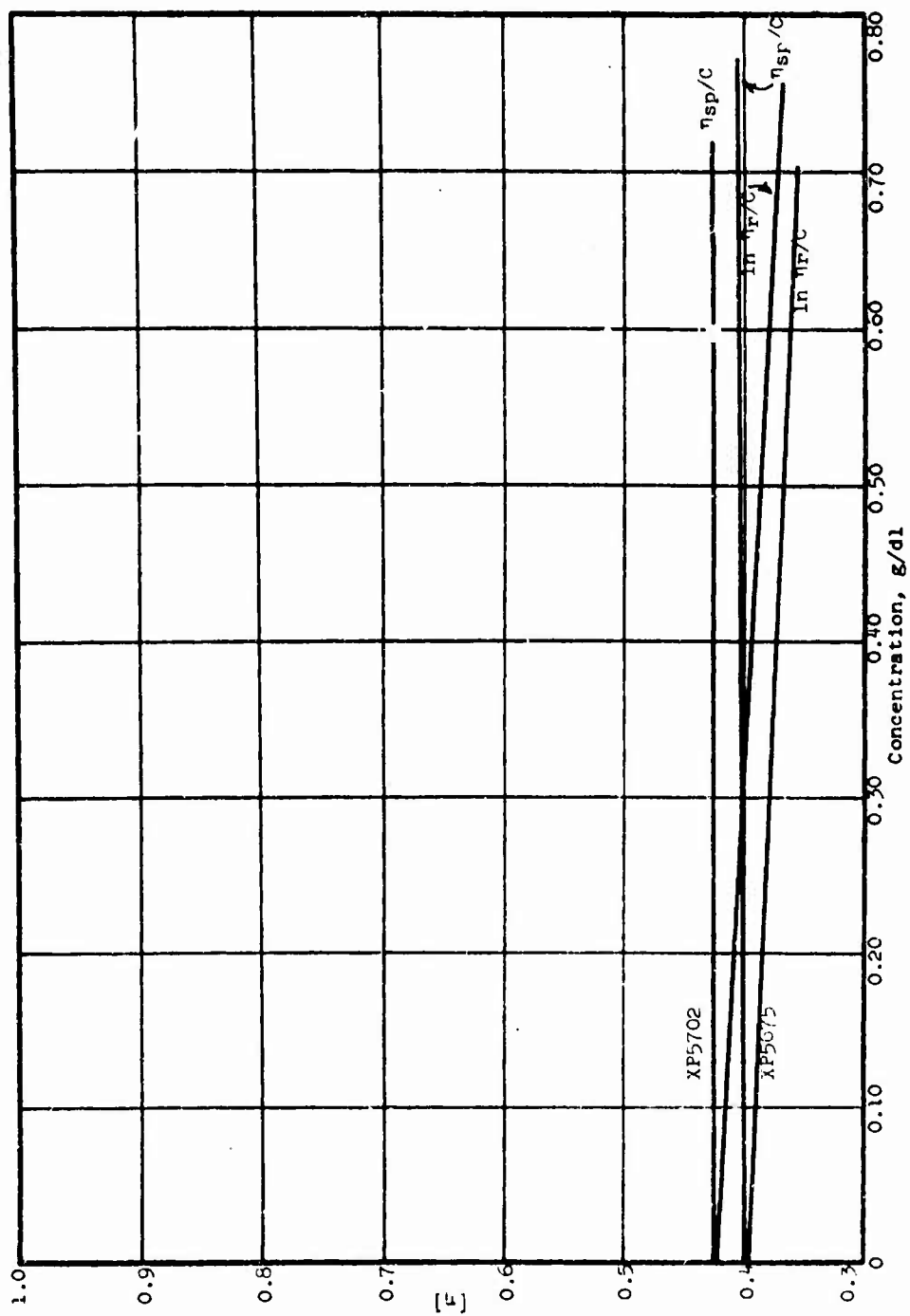


Figure 2. Reduced and Inherent Viscosities of XP5702 and XP5675 $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymers in Freon 113 at 35°C.

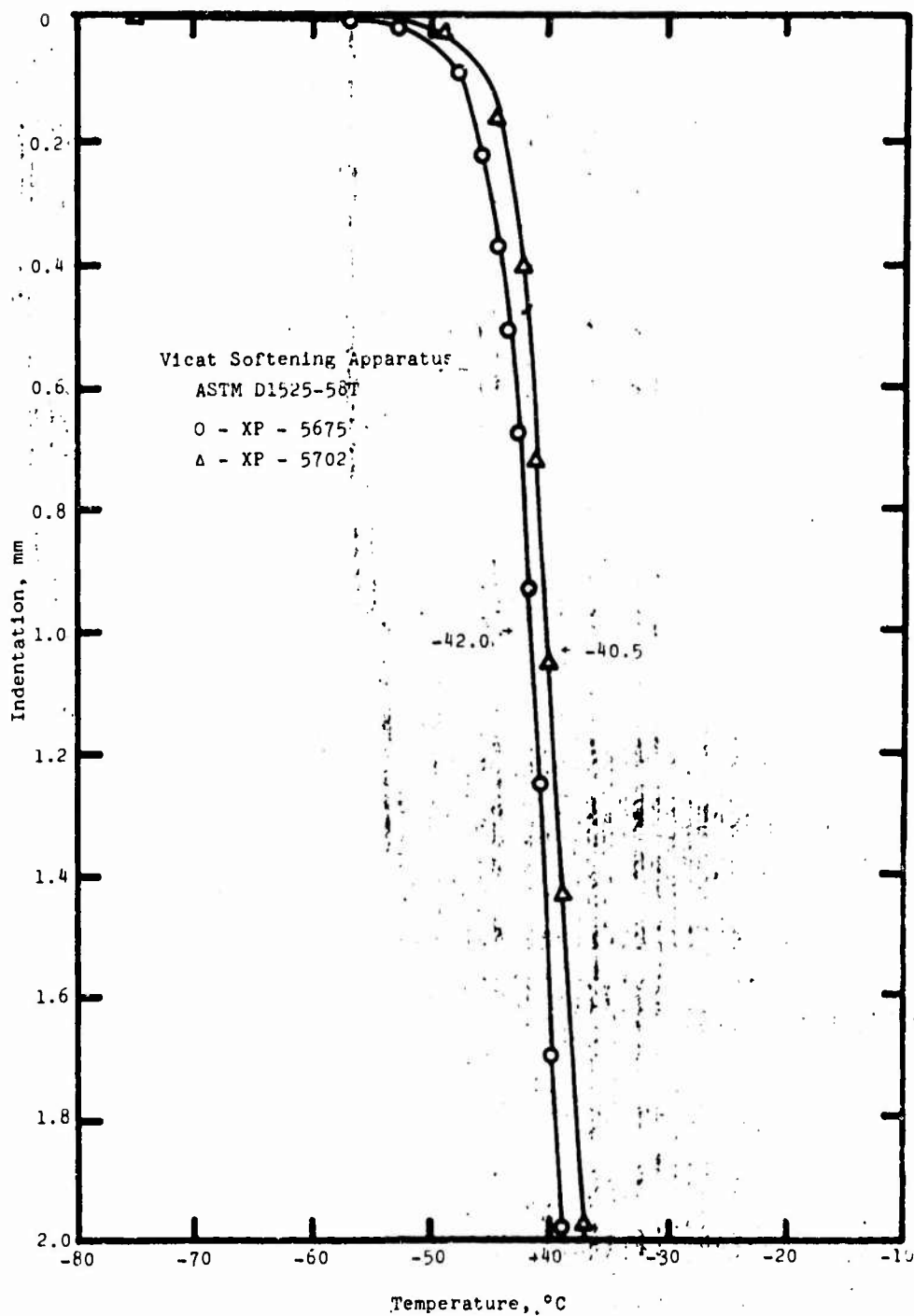


Figure 3. Vicat Softening Temperatures for XP5675 and XP5702 $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymers as Received.

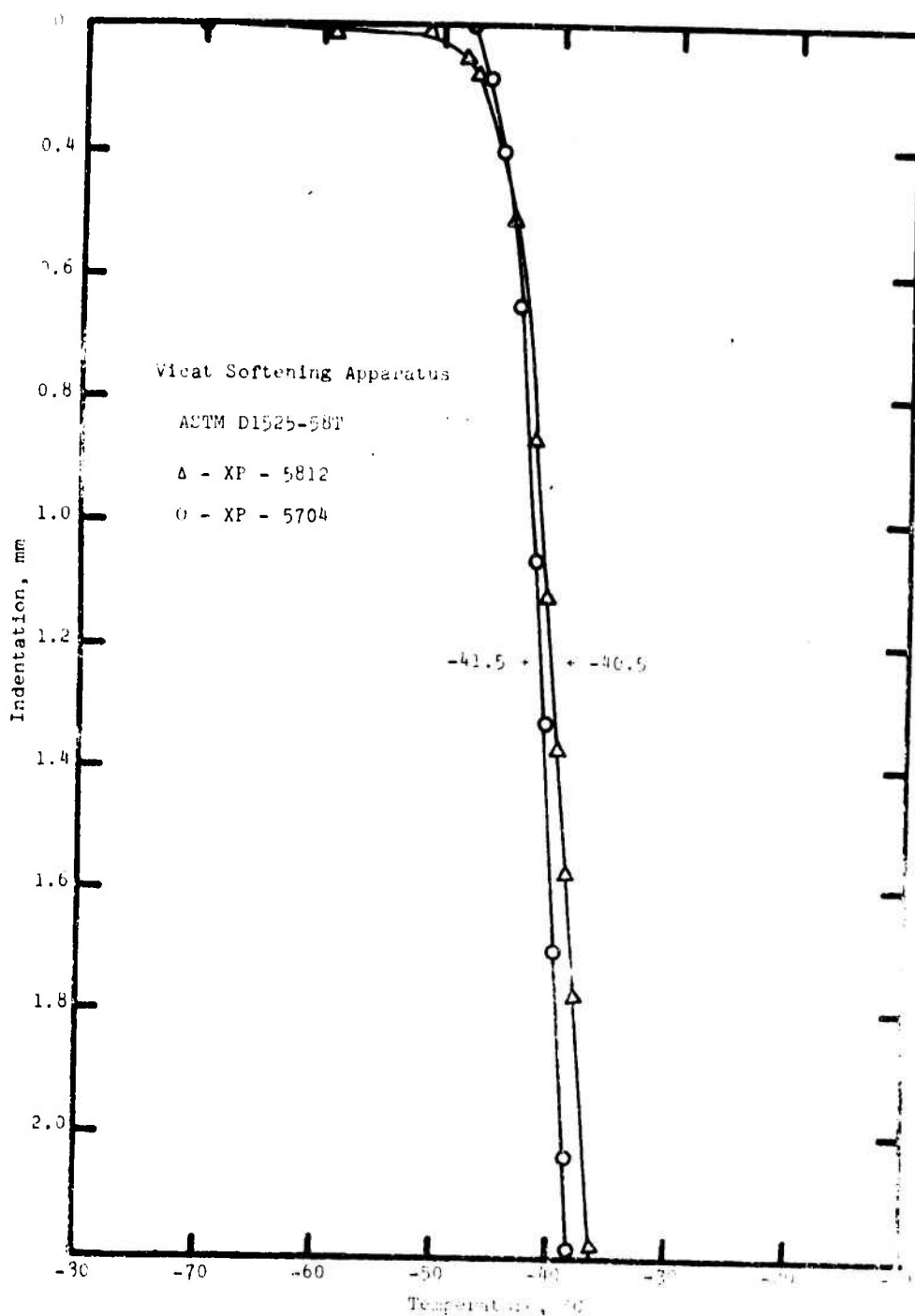


Figure 4. Vicat Softening Temperatures of XP5812 and XP5704 $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymers As Received.

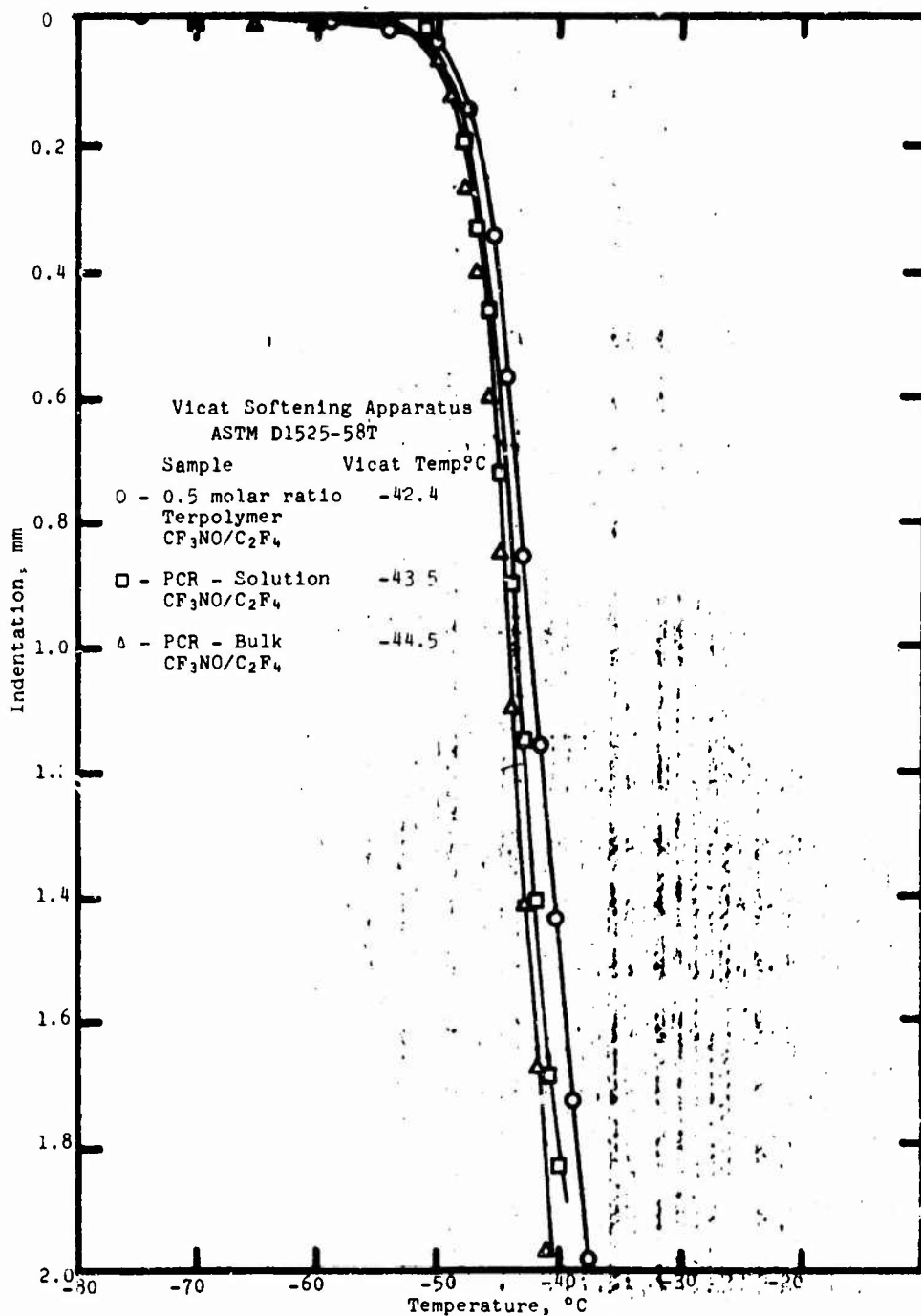


Figure 5. Vicat Softening Temperatures of 0.5 Molar Ratio $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Terpolymer, PCR-Solution, and PCR-Bulk $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymers.

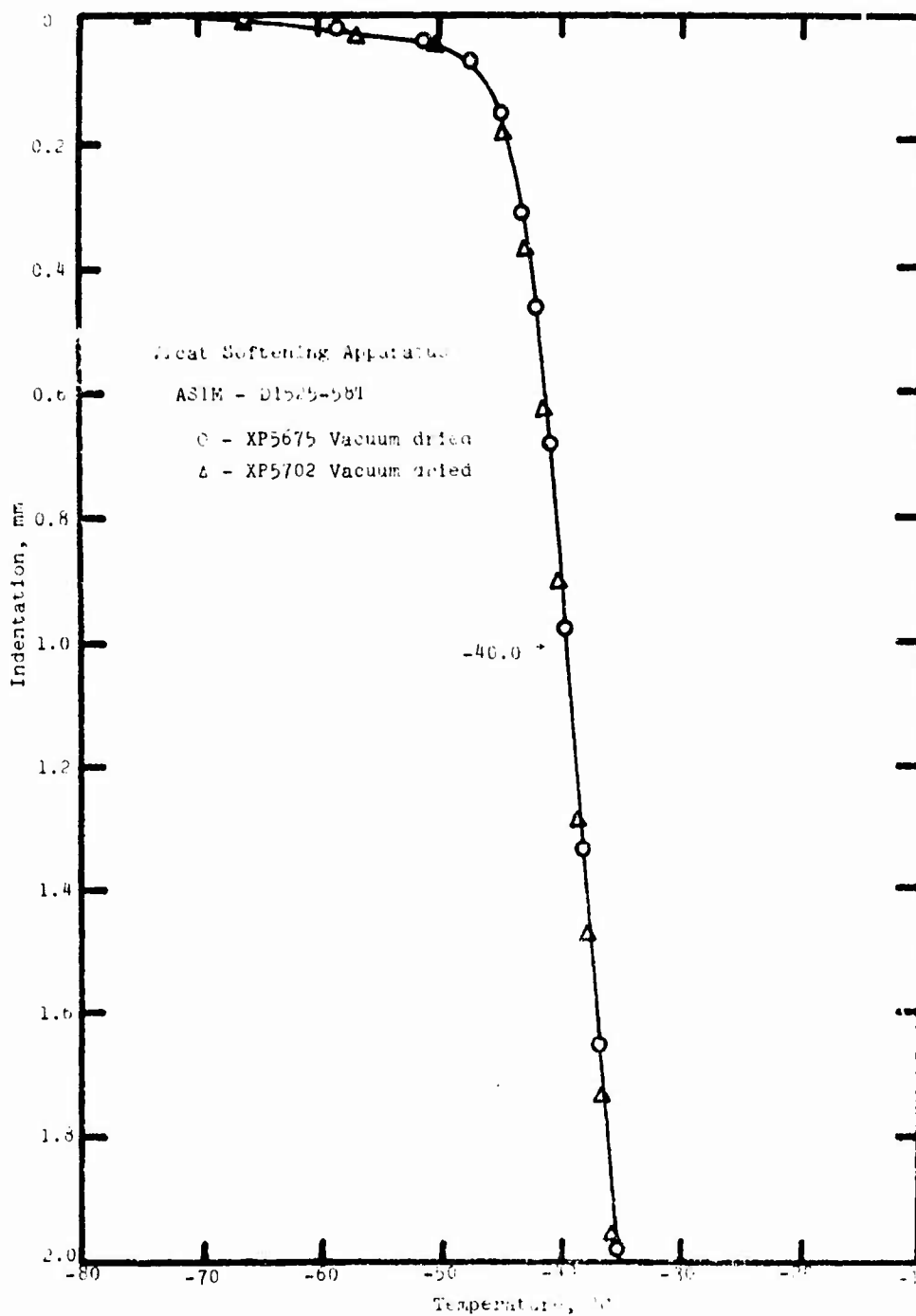


Figure 6. Vicat Softening Temperature for Vacuum Dried XP5675 and XP5702 $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymers.

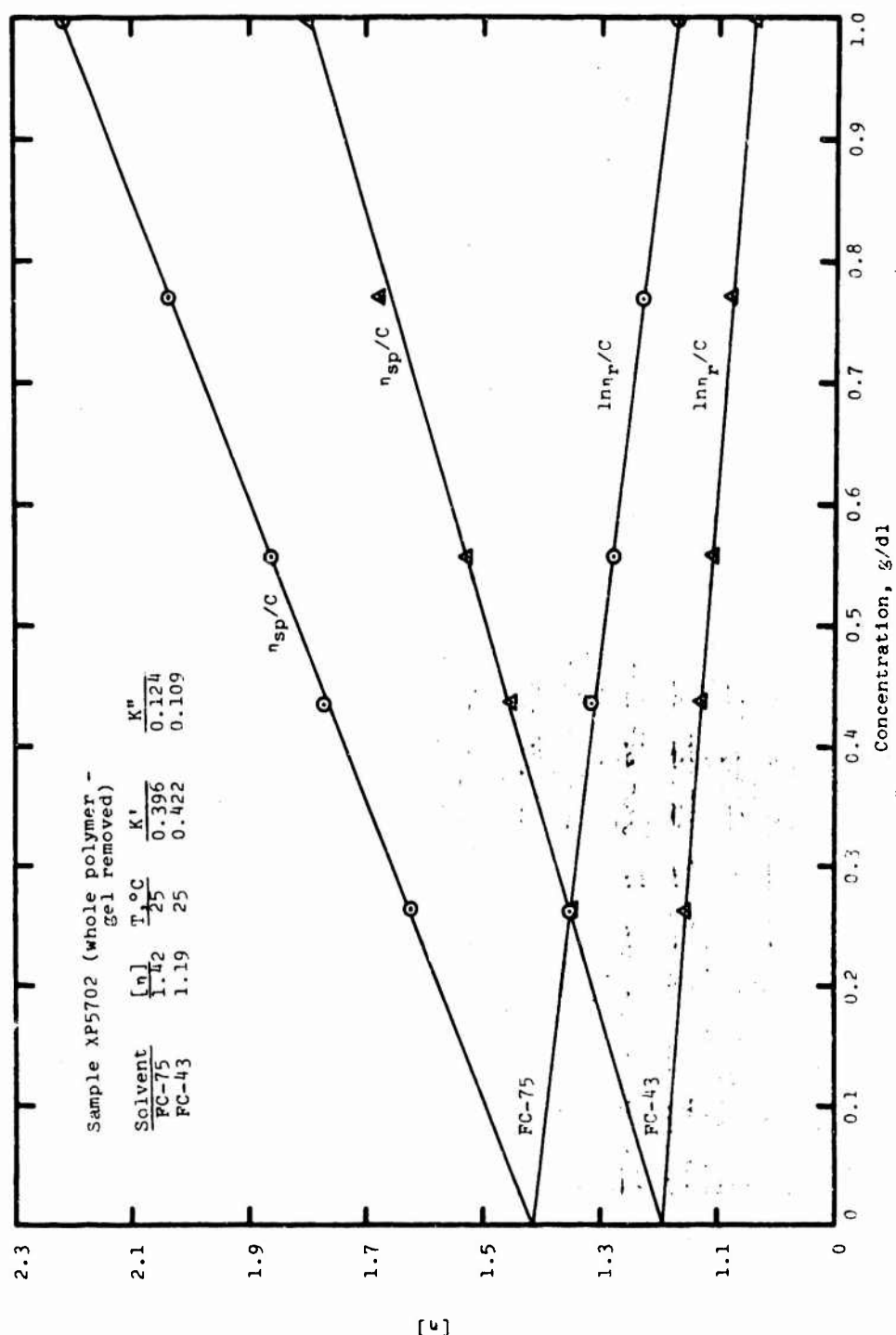


Figure 7. Reduced and Inherent Viscosities of the XP5702 $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymer in FC-75 and FC-43 Fluorocarbon Solvents at 25°C .

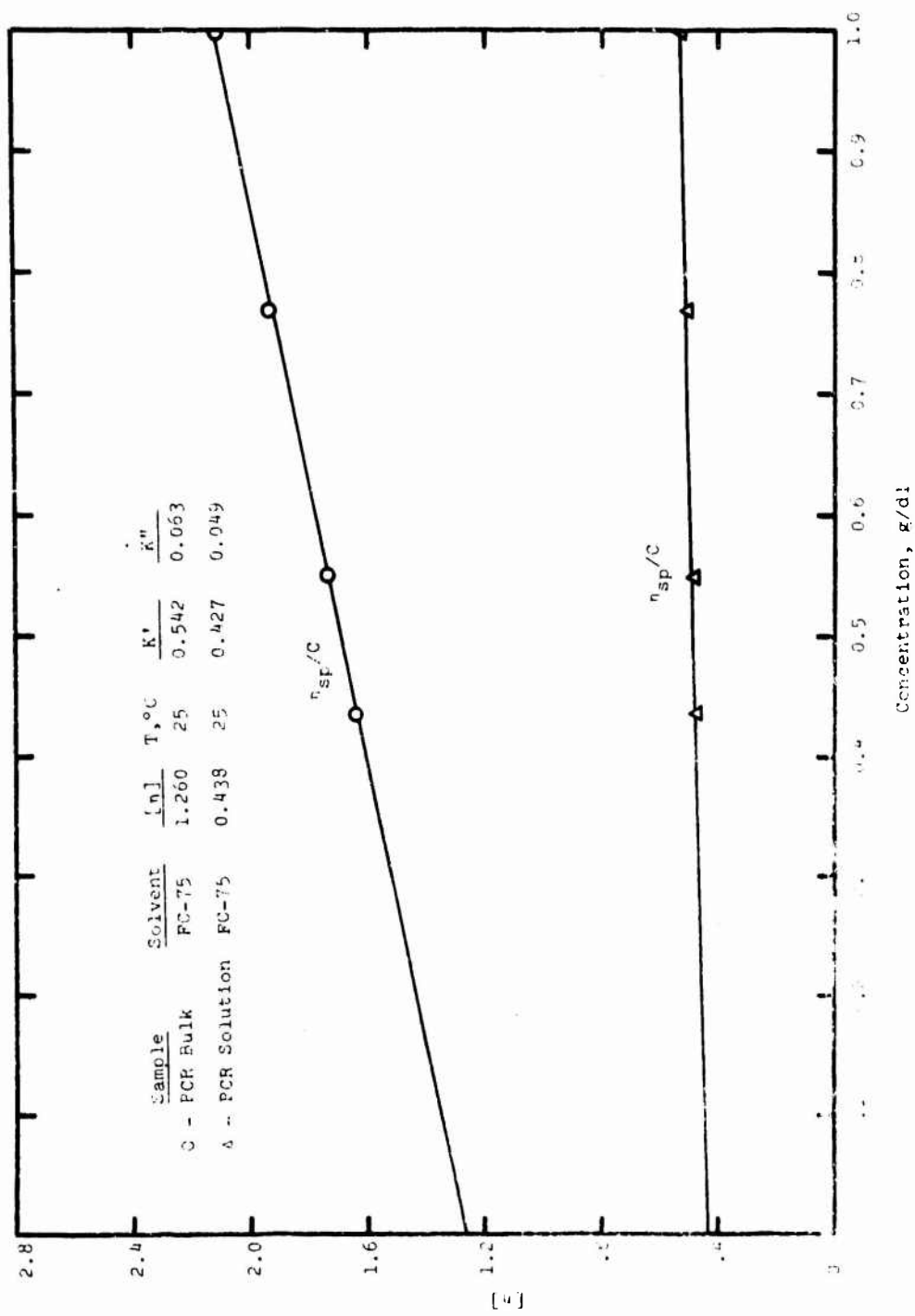


Figure 3. Reduced Viscosities of the PCR-Bulk and PCR-Solution
 CP-60/CP-75 Copolymers in FC-75 Fluorocarbon Solvent at 25°C.

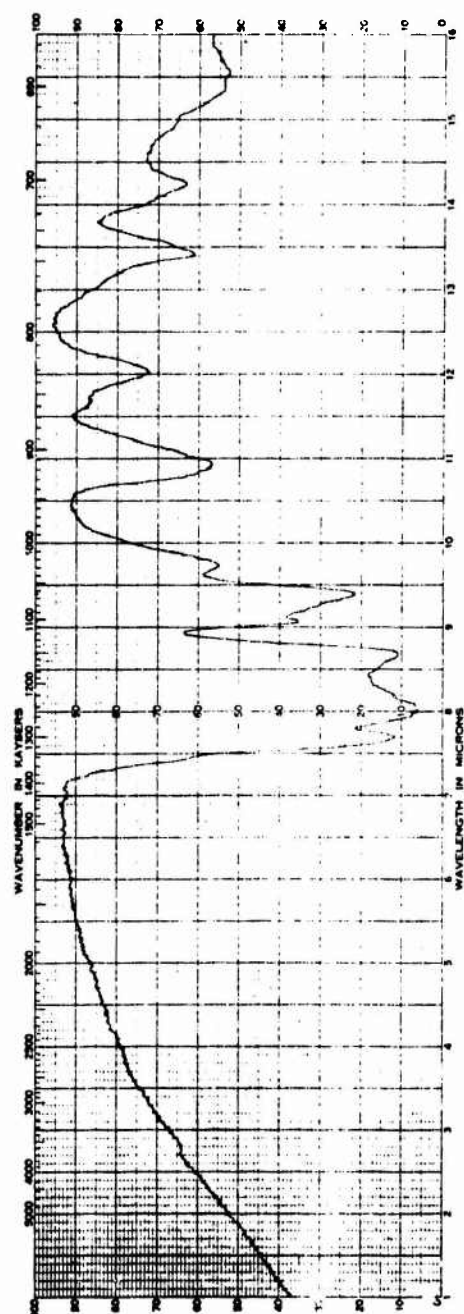


Figure 9. Infrared Spectrum of the $\text{CF}_3\text{NO/C}_2\text{F}_4$ Gum Sample XP5675.

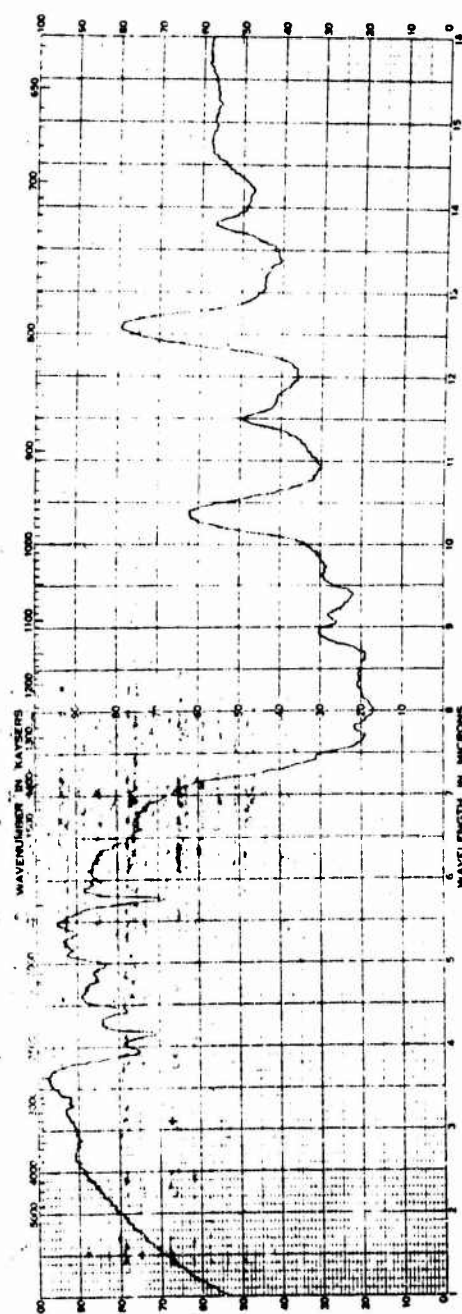


Figure 10. Infrared Spectrum of the $\text{CF}_3\text{NO/C}_2\text{F}_4$ Gum Sample XP5702.

File No. _____
Request No. 3612

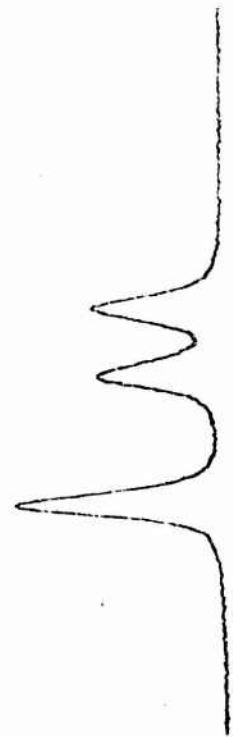
MONSANTO RESEARCH CORPORATION
Nuclear Magnetic Resonance File Card

Description and/or Formula NITROSO RUBBER ZR-561

RF Frequency 40.0 Mc
Nuclei F¹⁹

Sample No. ZR-561

Submitter	H. Wilson	Job No.	4505	Operator	JEC
Peak	1	2	3		
PPM	-11.5	+11.5+24.0			
Area Ratio	3.0	2.0	2.0		



Peak					
PPM					
Area Ratio					

Date Run: 12/21/64

Reference: Trichloroacetic Acid
Resolution: M-SH

INST. DATA:
RF Gain 4
RF Field 3 C 1 F
RF Current 10 uA
Sw. Freq. C
Sw. Field F
Attenuation X
Chart Speed 2 mm/Sec
Probe Invert mm
Spike Tube mm
Sweep Rate Fast 100

Reference: M-SH
Resolution:
INST. DATA:
RF Gain C
RF Field F
RF Current uA
Sw. Freq. C
Sw. Field F
Attenuation X
Chart Speed mm/Sec
Probe Invert mm
Spike Tube mm
Sweep Rate

Figure 11. Nuclear Magnetic (F19) Resonance Spectrum of The CF3NO/C2F4 Gum Sample XP5575.

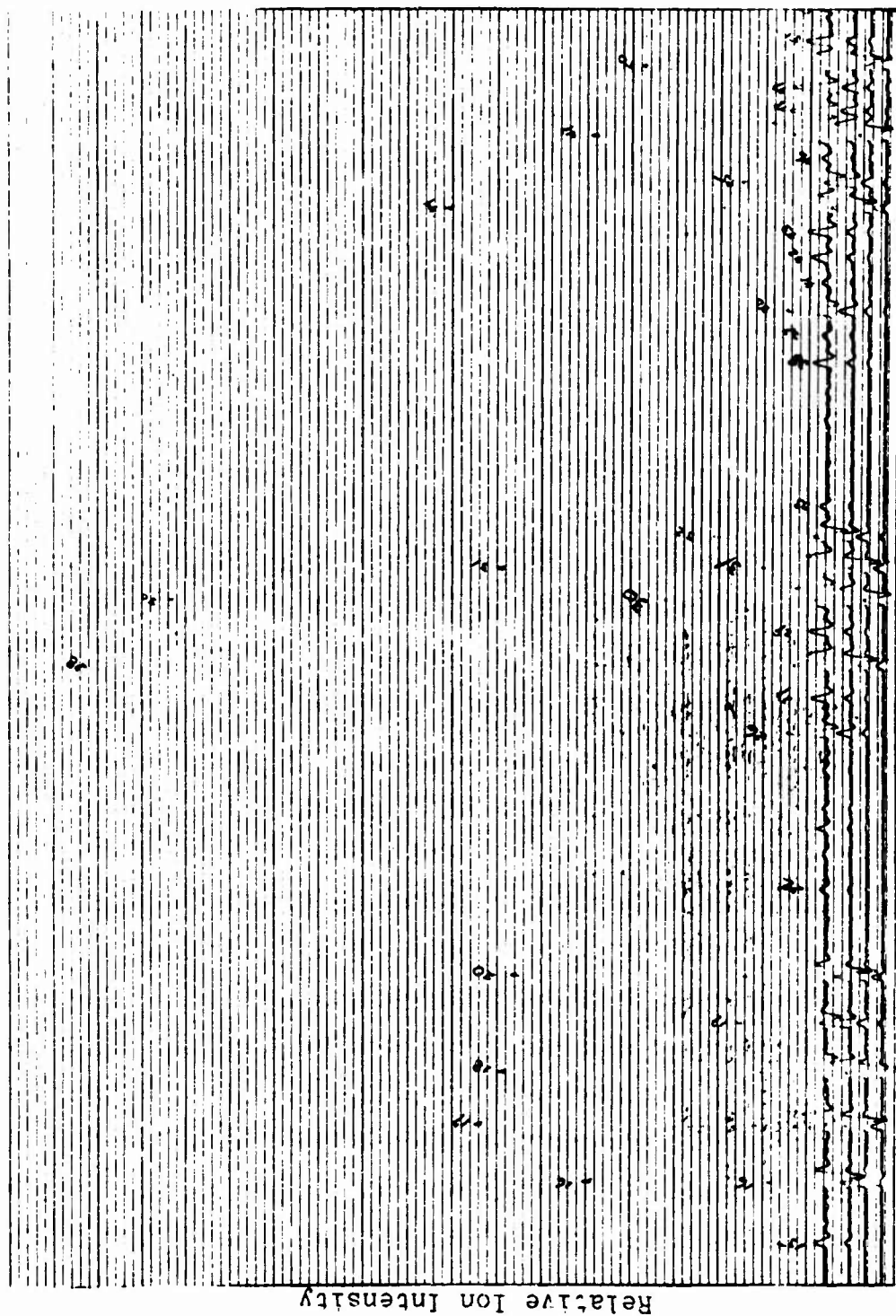


Figure 12. Actual Mass Spectra From Mass 15 to 50 For XP5675
 $\text{CF}_3\text{NO/C}_2\text{F}_4$ Gum (100°C).

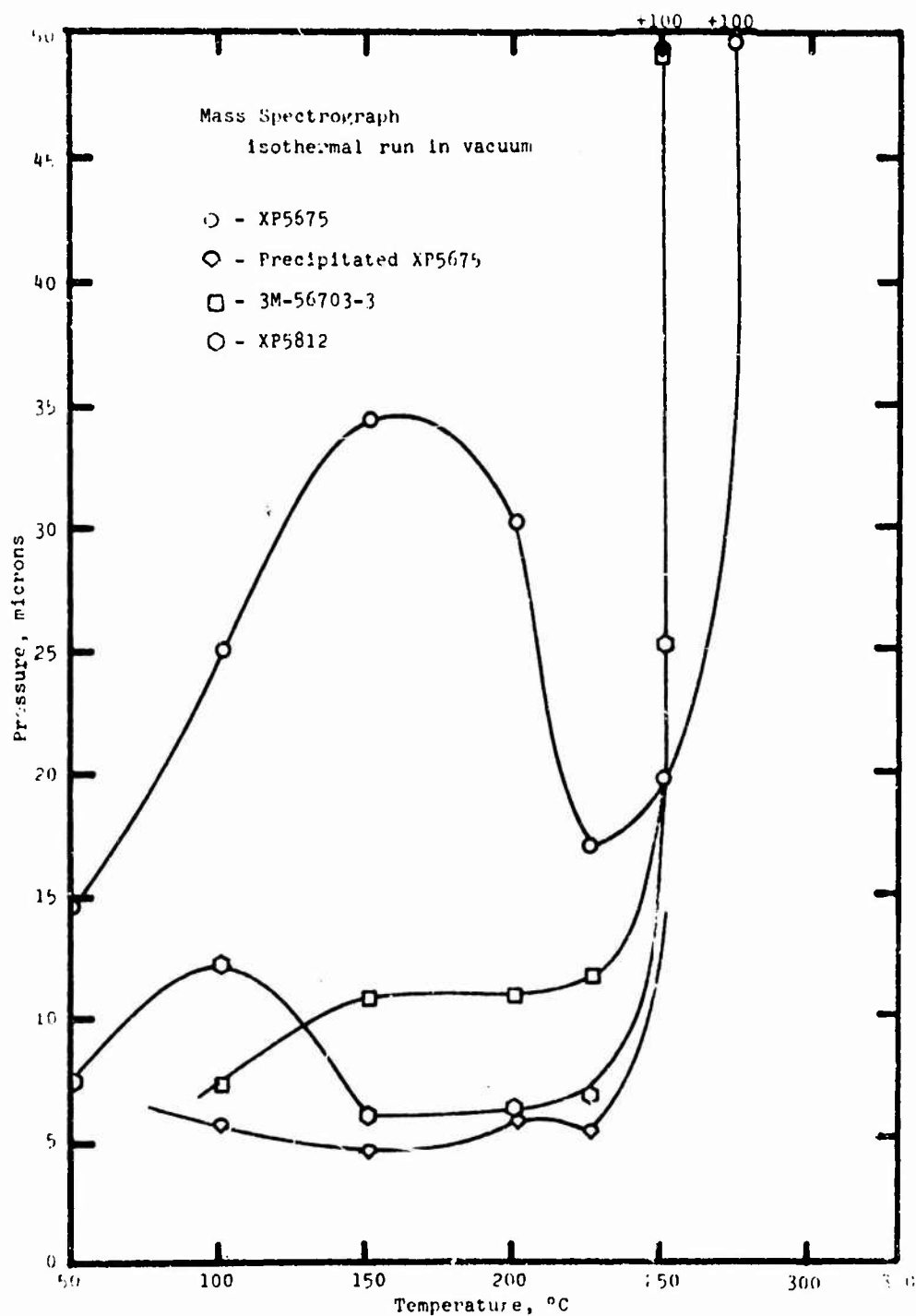


Figure 13. Mass Spectrograph Pressure During Isothermal Runs on Samples XP5675, Vacuum-Dried XP5675, 3M-56703-3, and XP5812.

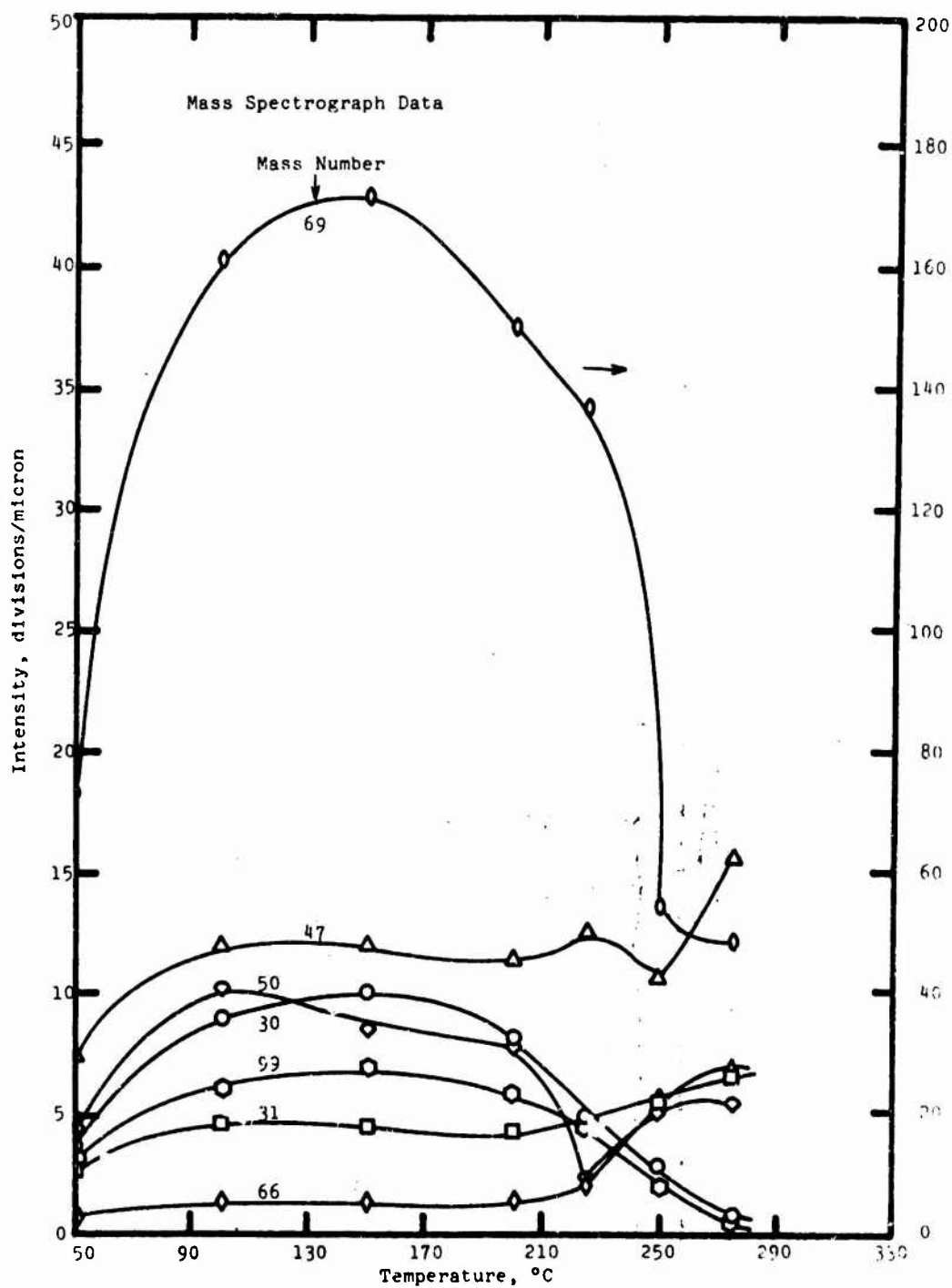


Figure 14. Most Prominent Ionic Species From 50 up to 275°C of Sample XP5675.

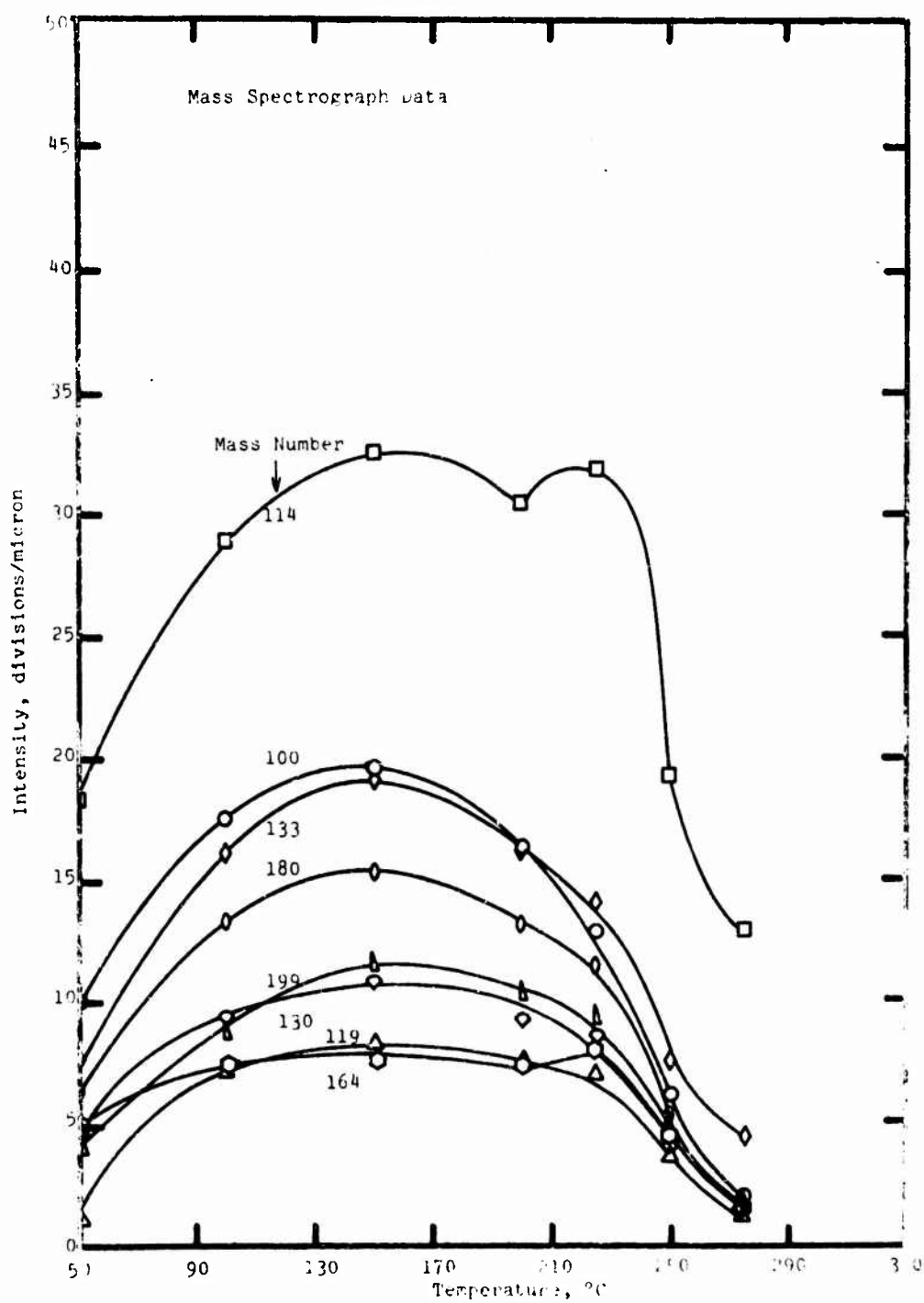


Figure 15. Most Prominent Ionic Species From 50 Up to 275°C of Sample XP5675.

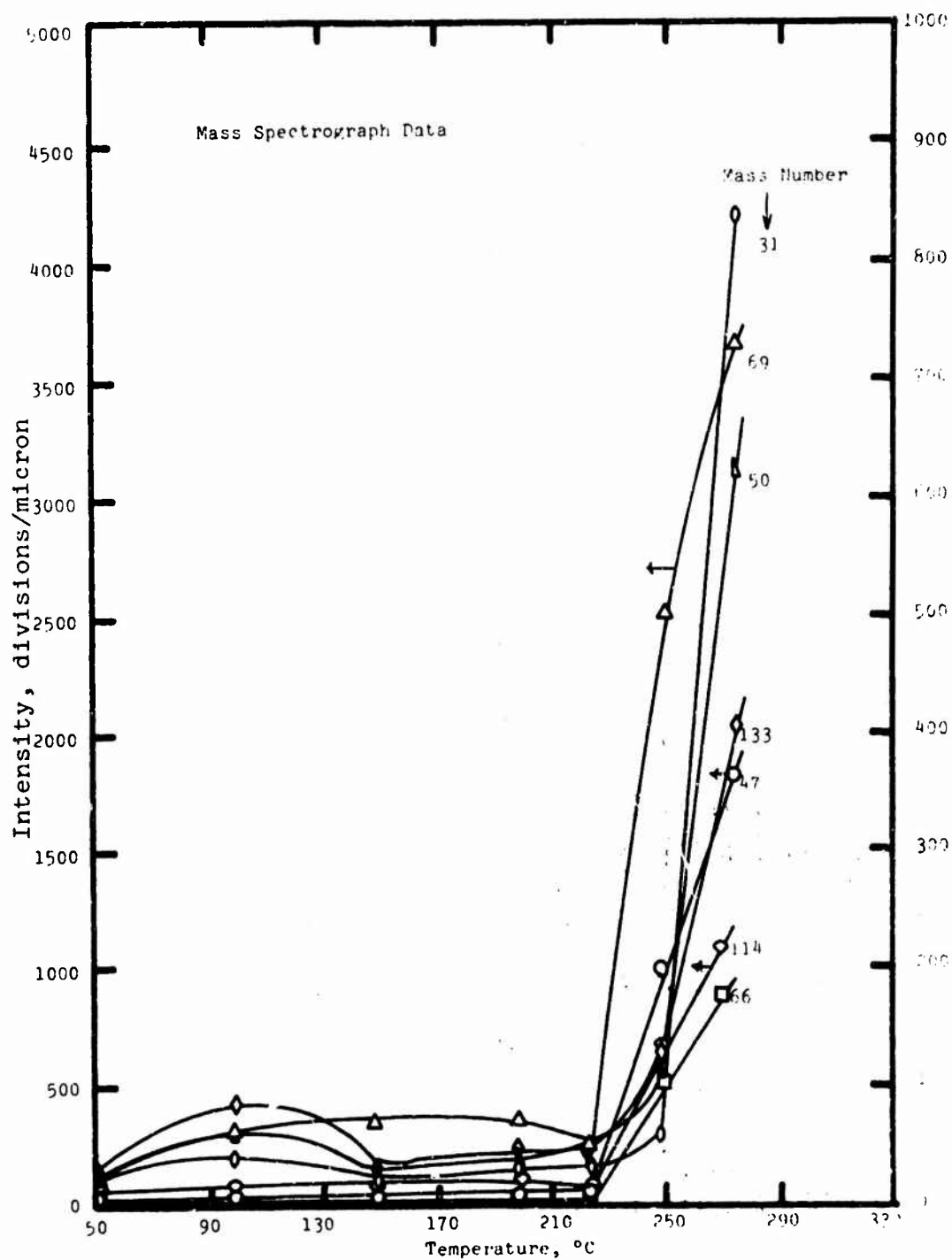


Figure 16. Most Prominent Ionic Species From 50 Up to 275°C of Sample of Vacuum-Dried XP5675.

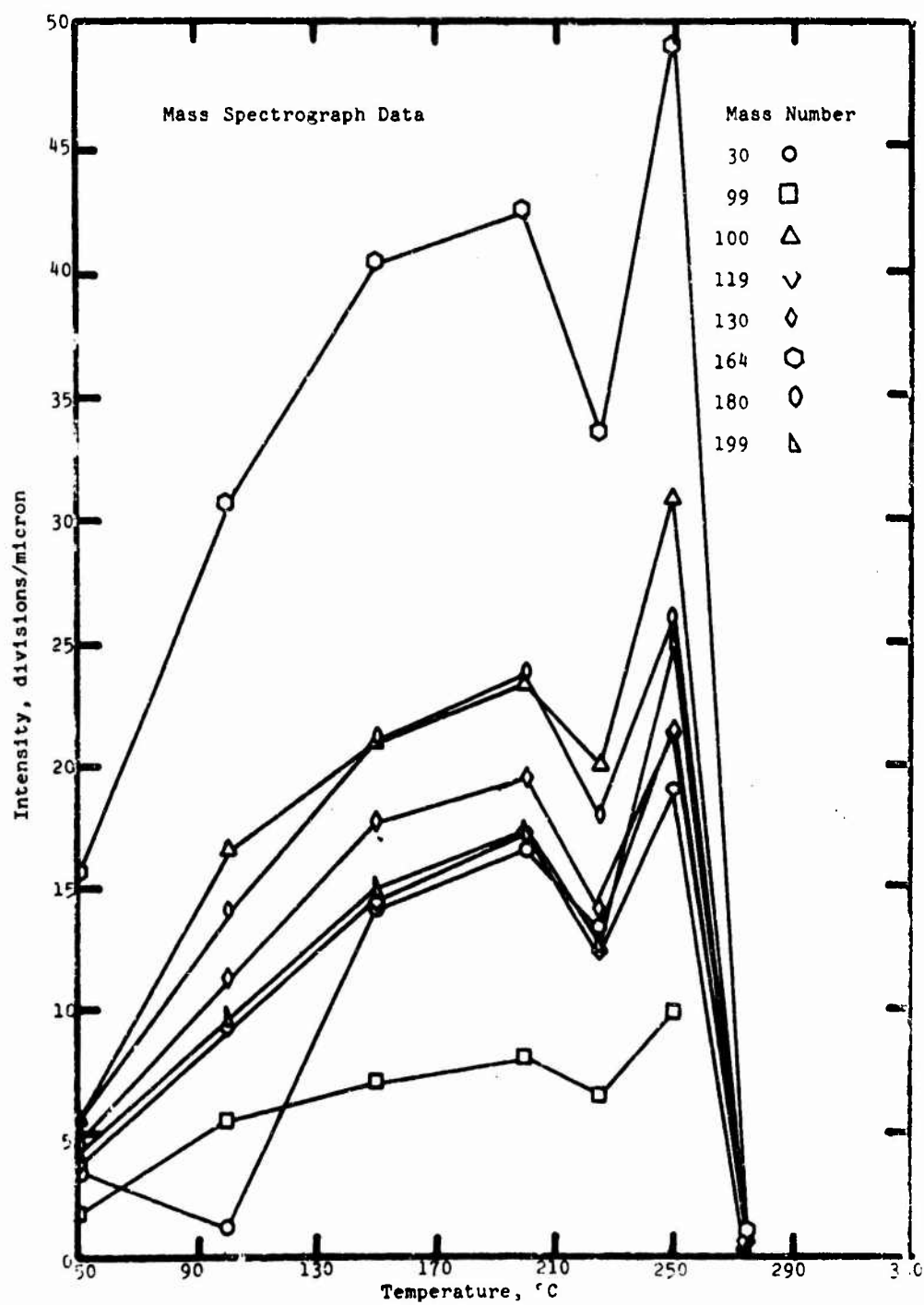


Figure 17. Most Prominent Ionic Species From 50 Up to 275°C of Sample of Vacuum-Dried XP5675.

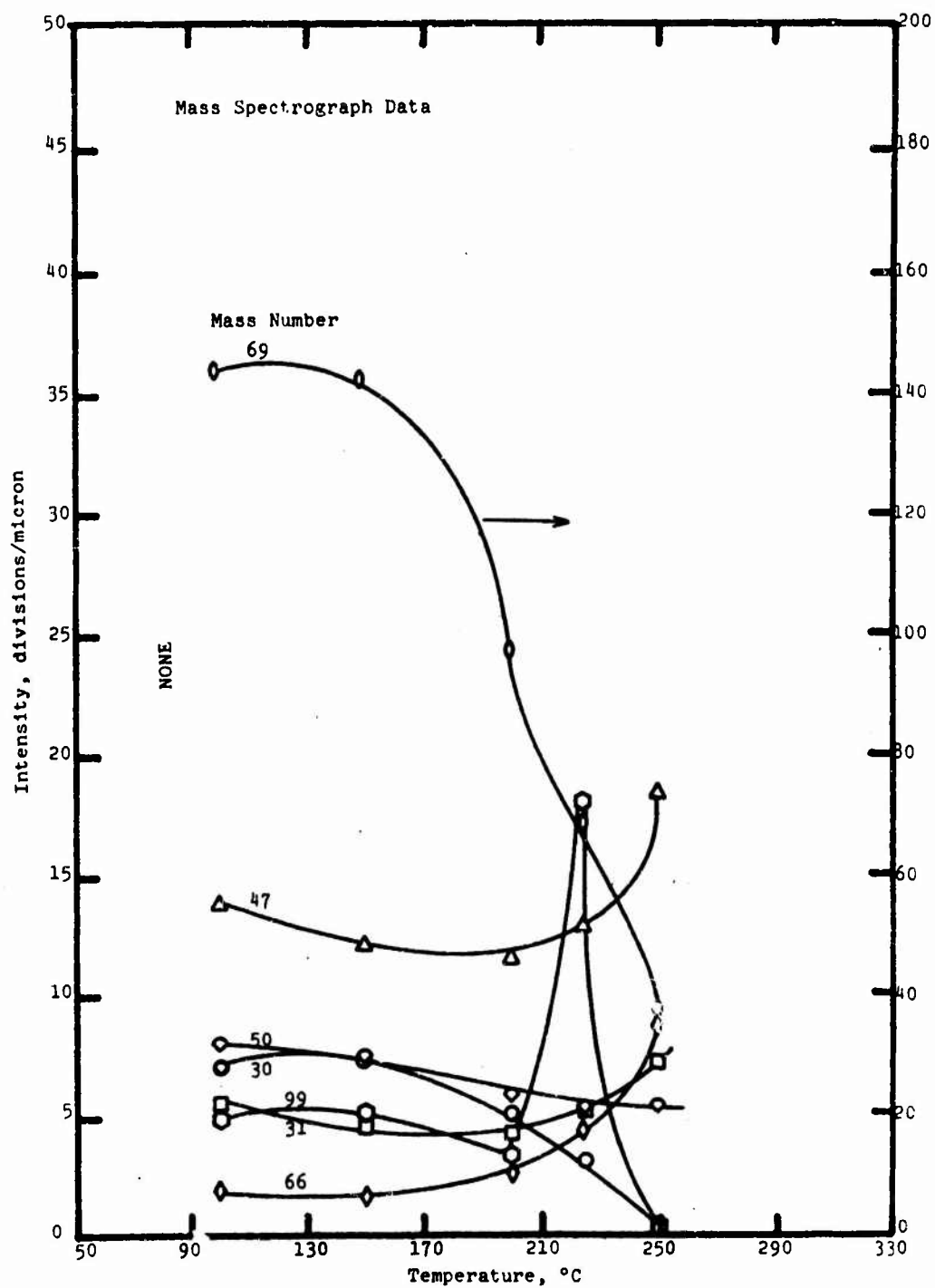


Figure 18. Most Prominent Ionic Species From 50 Up to 250°C of Sample 3M-56703-3.

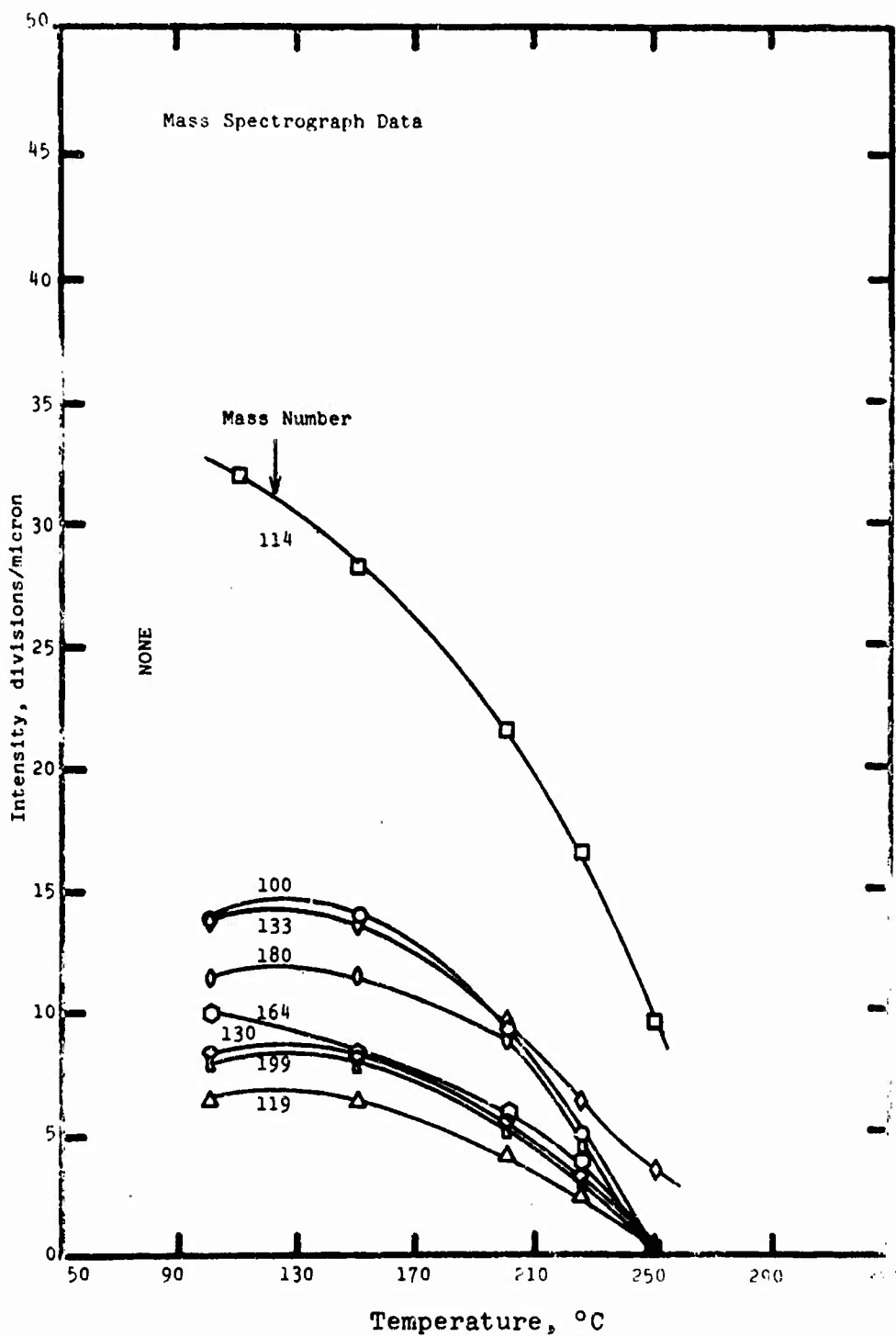


Figure 19. Most Prominent Ionic Species From 50 Up to 250°C of Sample 3M-56703-3.

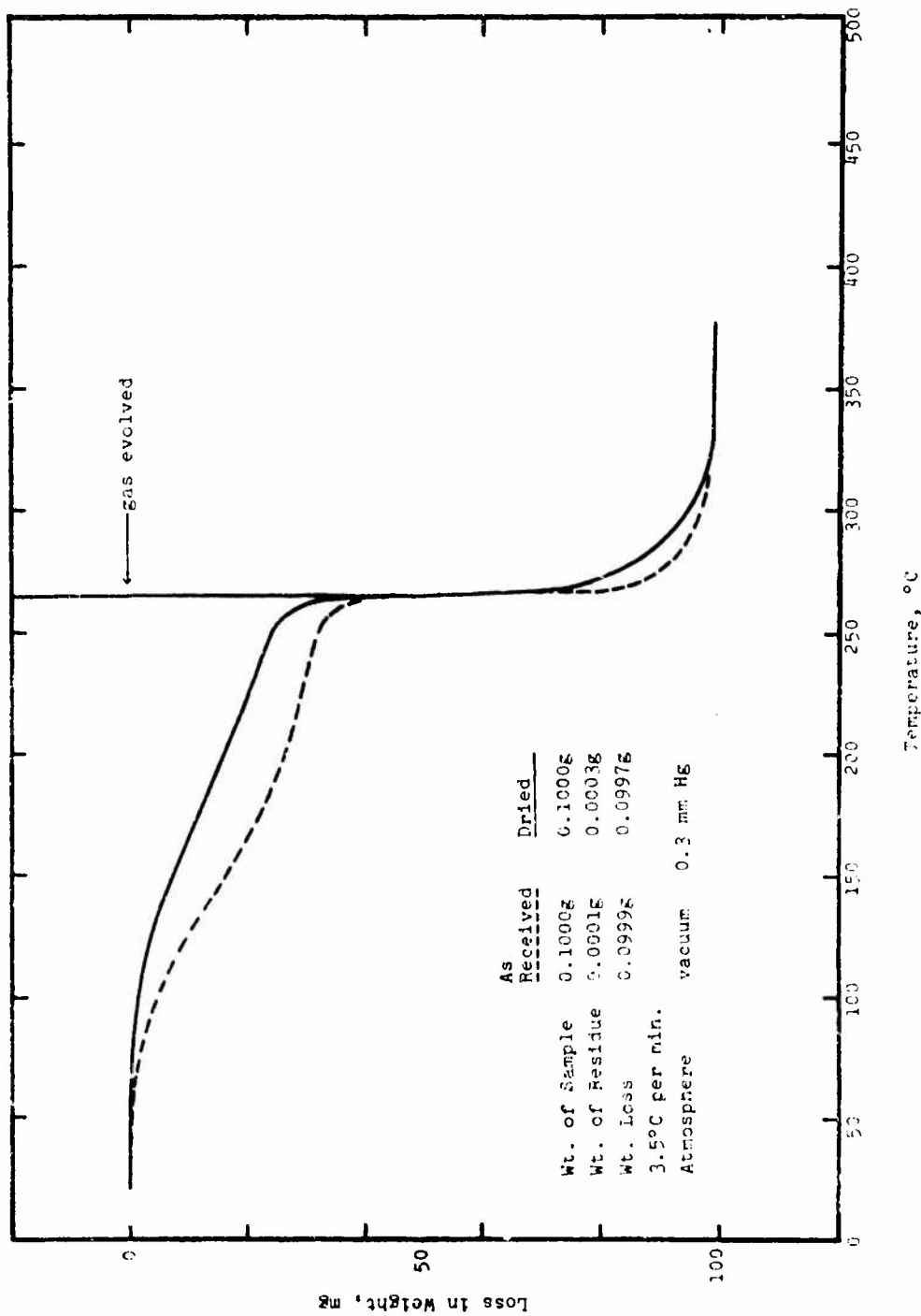


Figure 20. Thermogravimetric Analysis Curves for $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymer
Sample XP5675 Before and After Vacuum-Drying 16 Hours at 80°C .

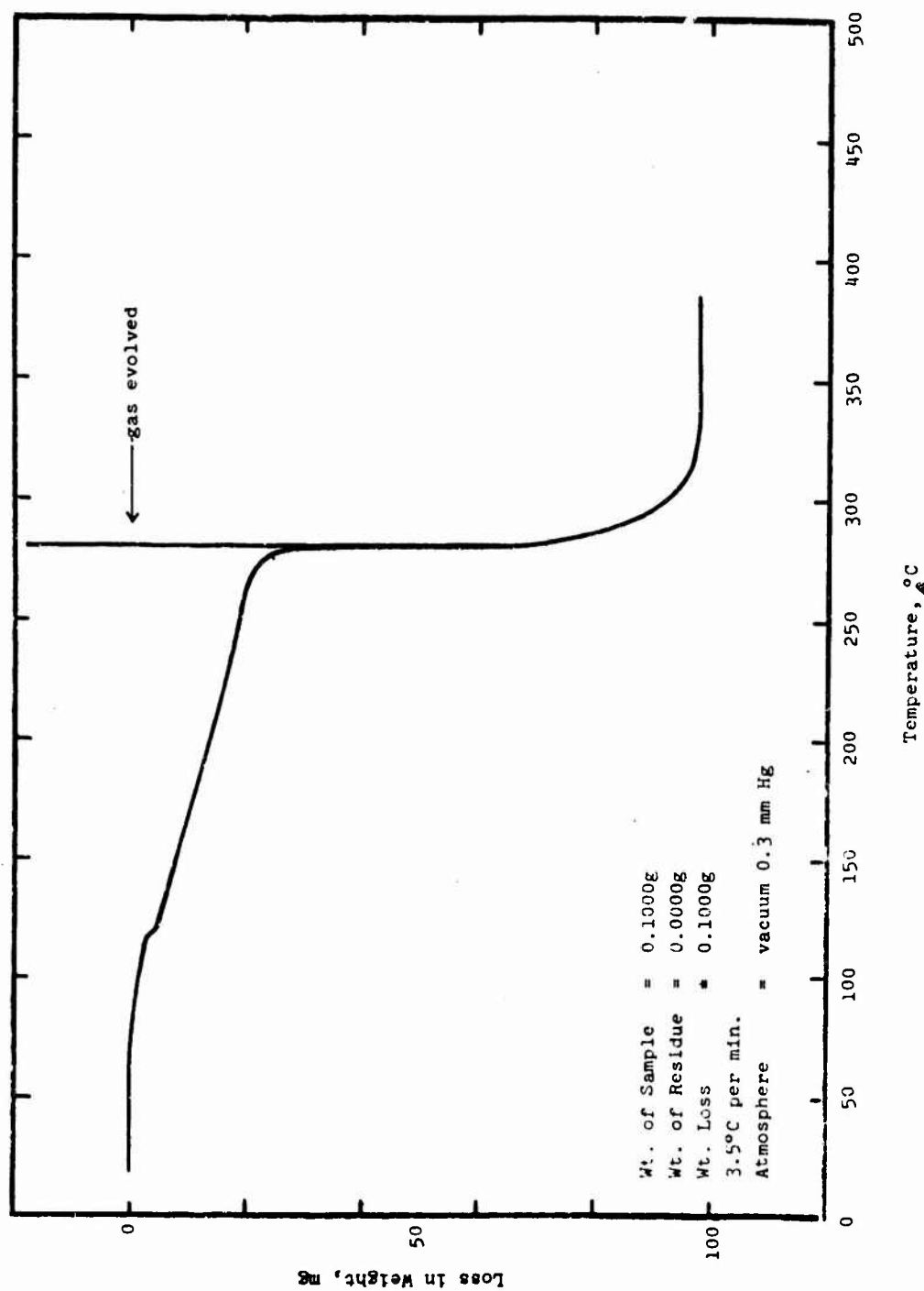


Figure 21. Thermogravimetric Analysis Curve for $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymer Sample 3M-56703-3.

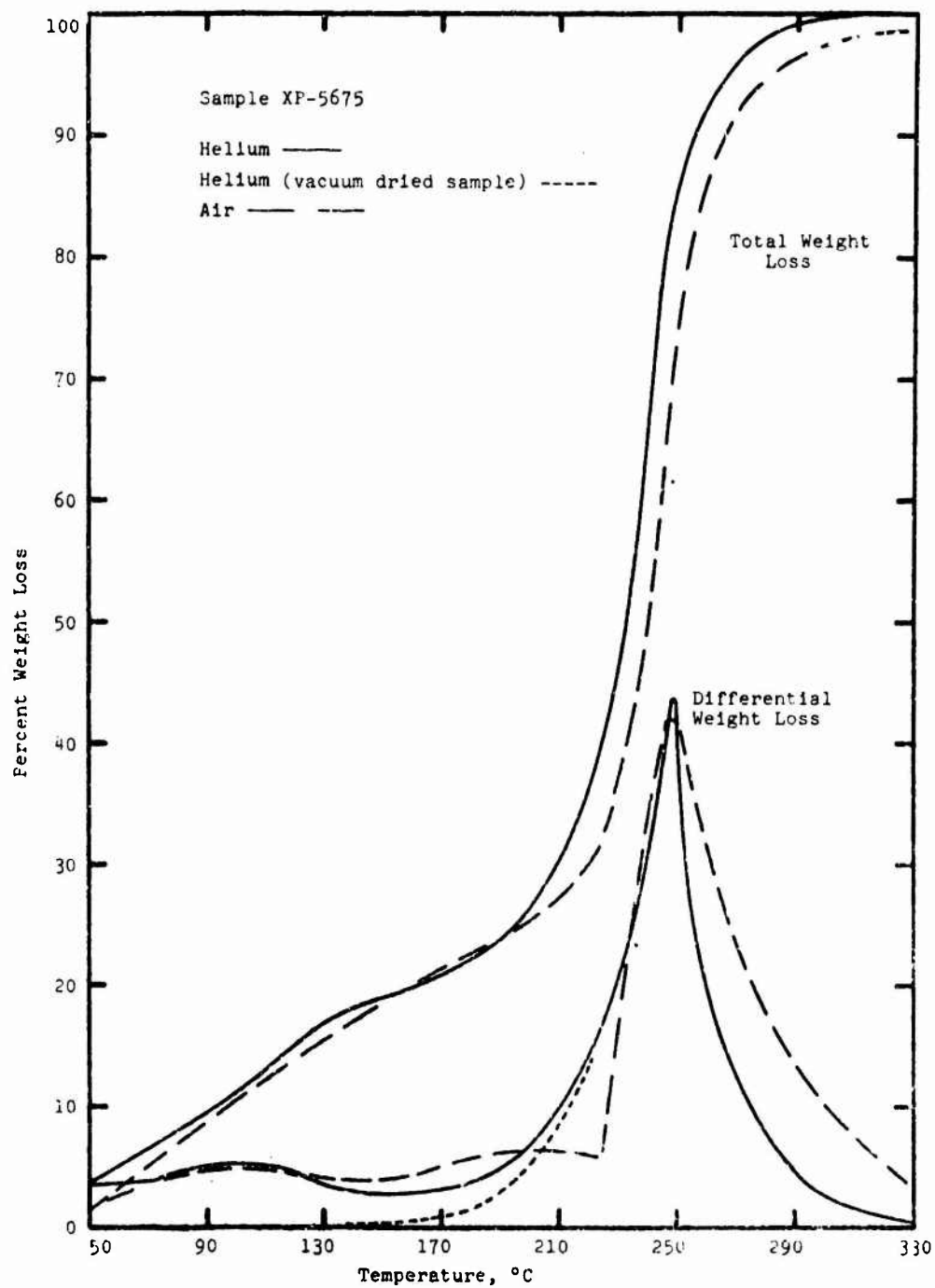


Figure 22. Composite of Total and Differential Weight Loss of $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymer Sample XP5675 in Helium and Air.

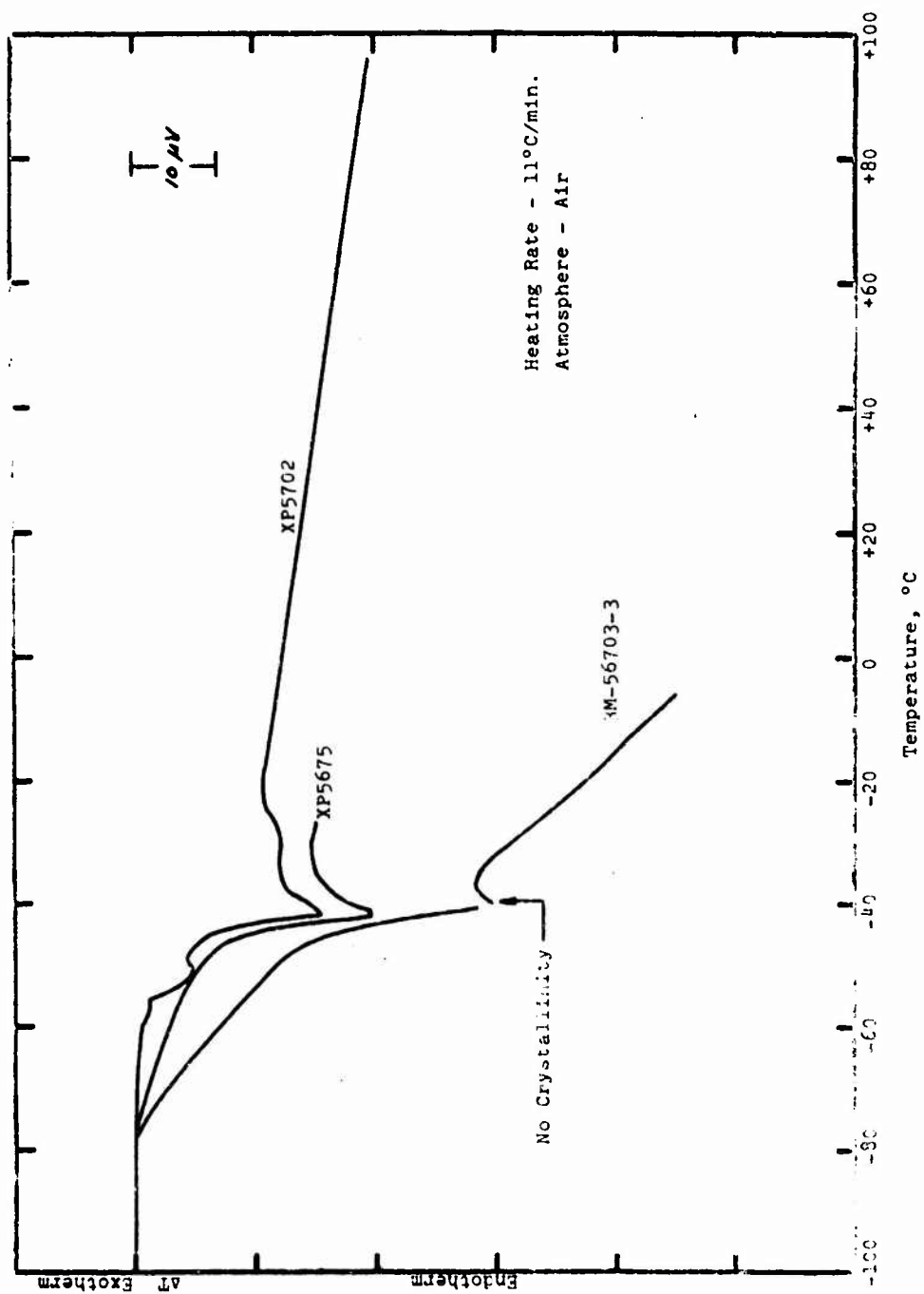


Figure 23. Differential Thermographs of three $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymers (low temperature).

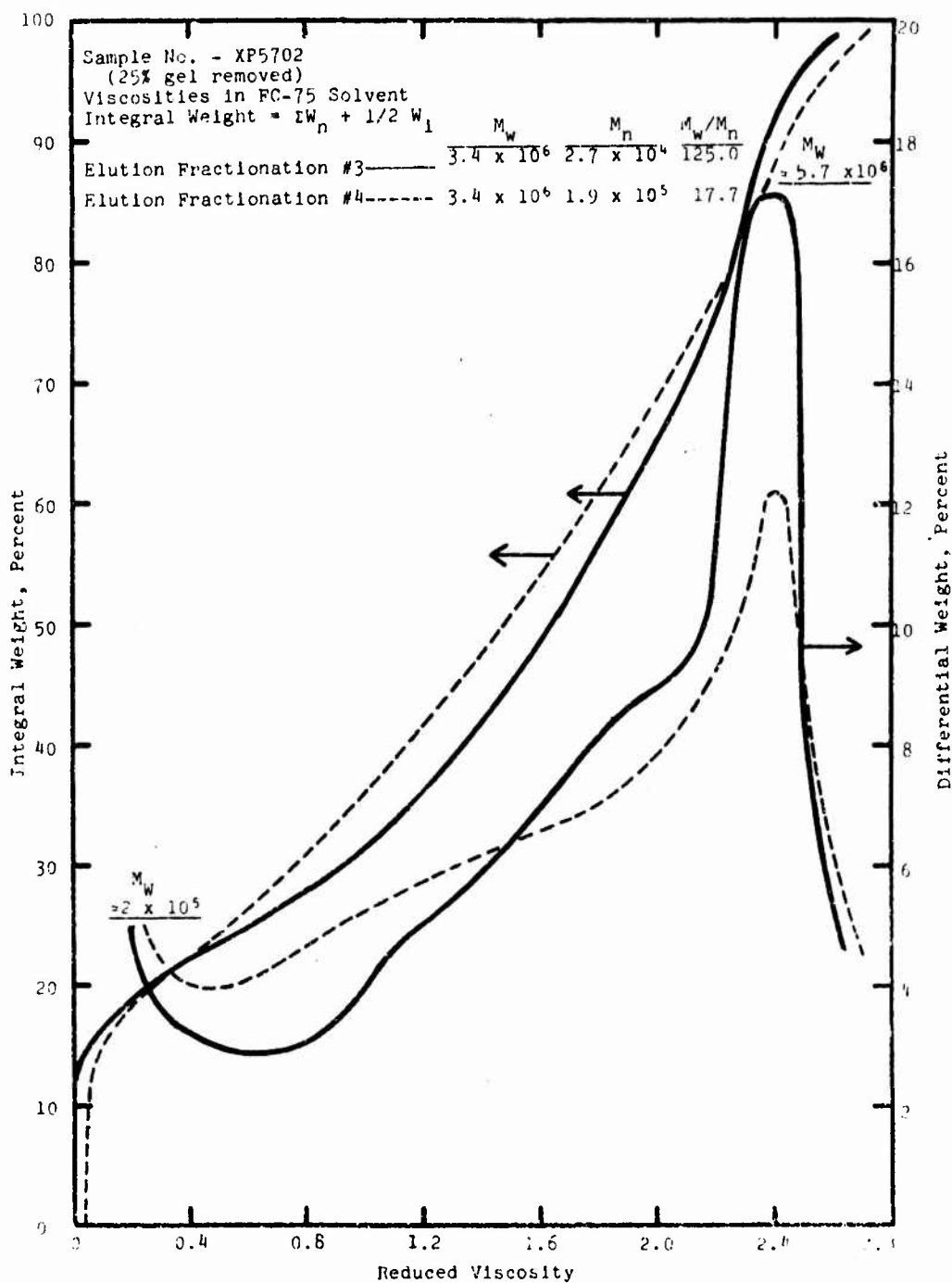


Figure 24. Total and Differential Weights As A Function of Viscosity For The $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymer XP5702 Elution Fractionation #3 and #4.

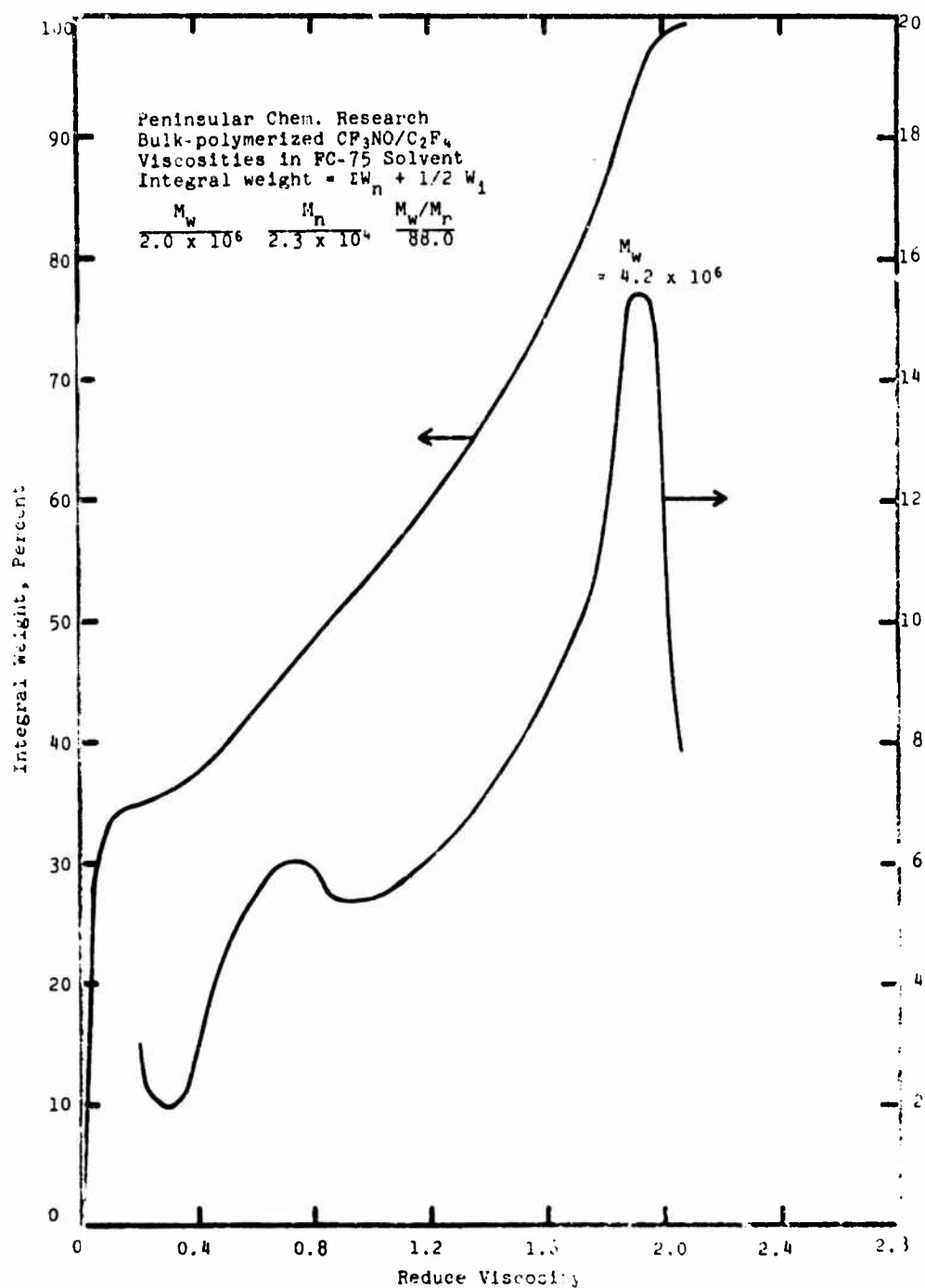


Figure 25. Total and Differential Weights As A Function of Viscosity For The Peninsular ChemResearch Bulk-Polymerized $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymer.

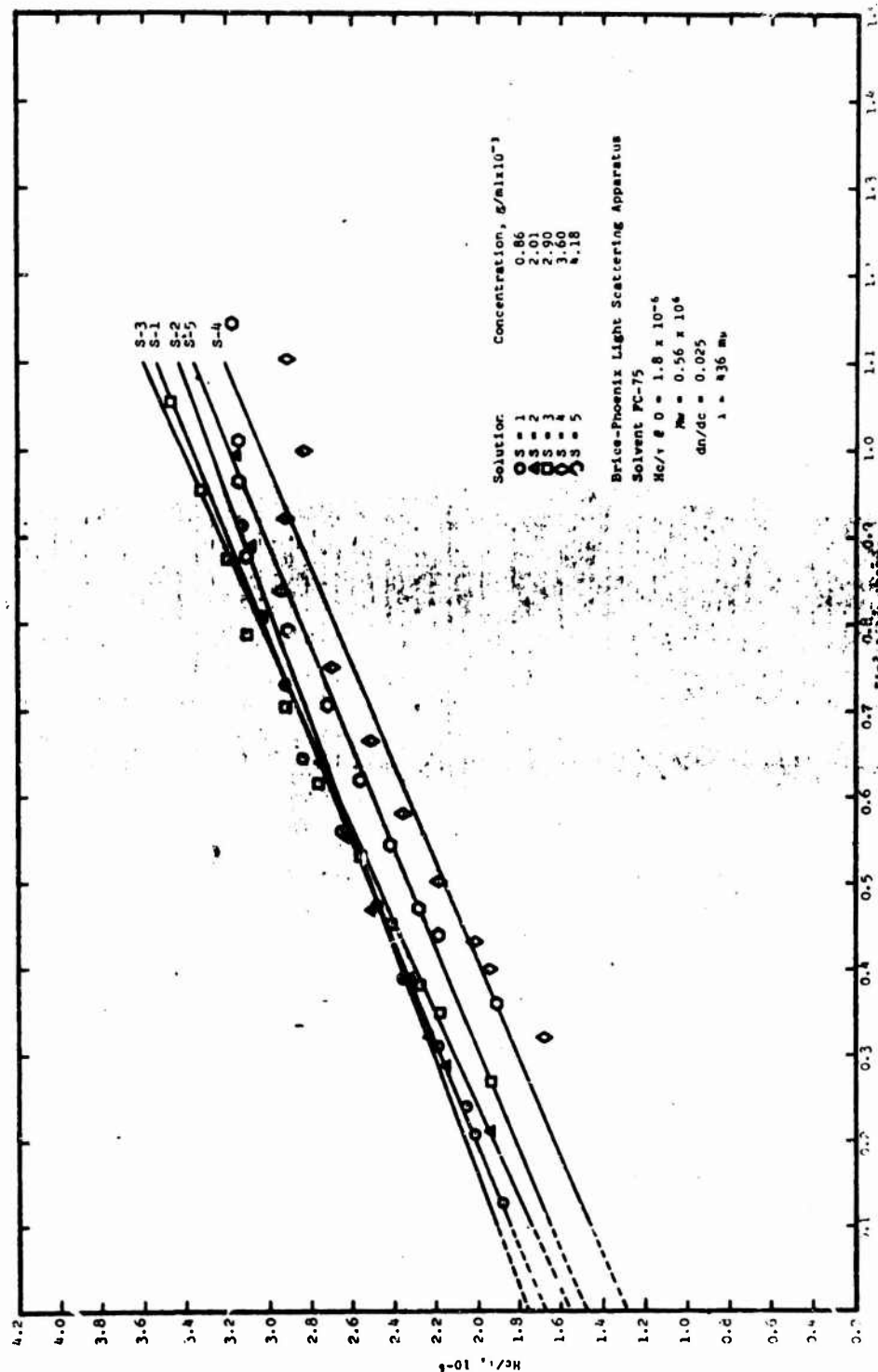


Figure 26. Zimm Plot of $\text{CF}_3\text{NO/C}_2\text{F}_4$ Copolymer Sample 3M-56703.

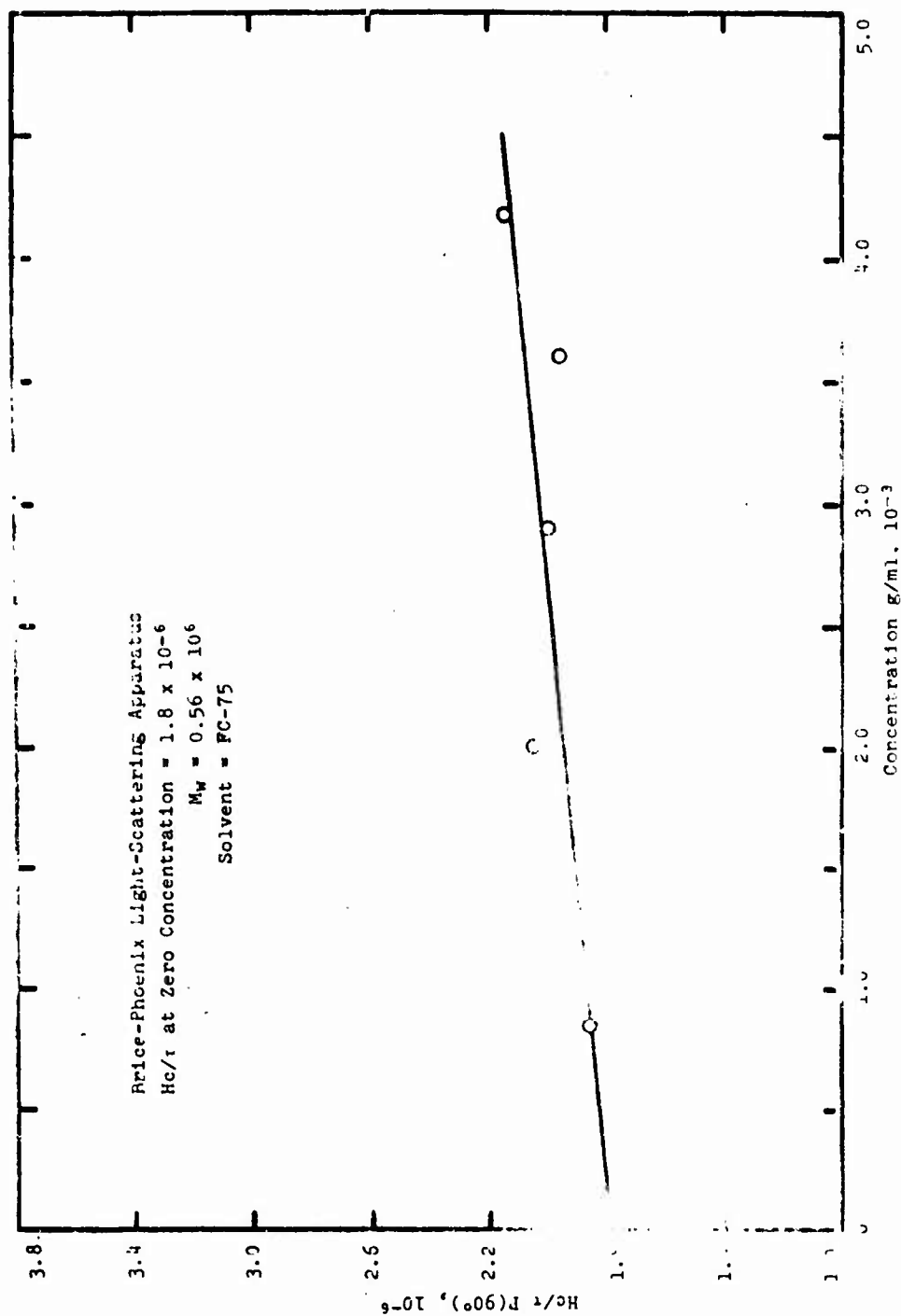


Figure 27. $H_c/\tau P(90^\circ)$ Versus Concentration For The
 CF_3NO/C_2F_4 Copolymer Sample 3M-56703.

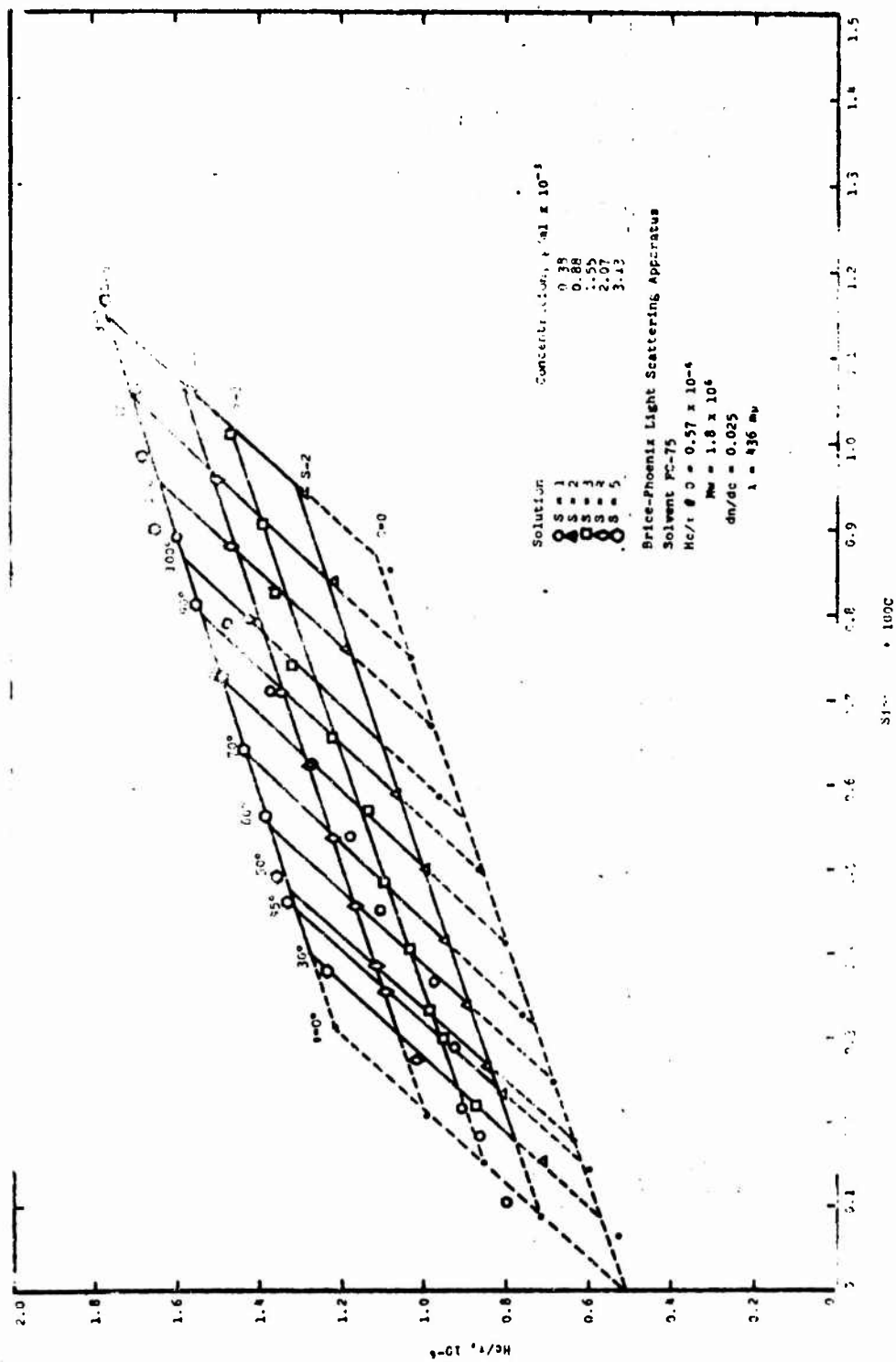


Figure 10. Dependence of dn/dc on C for CF_3NO/C_2F_4 Copolymer Fraction No. 4, Run No. 2, Thiokol Sample XP5702.

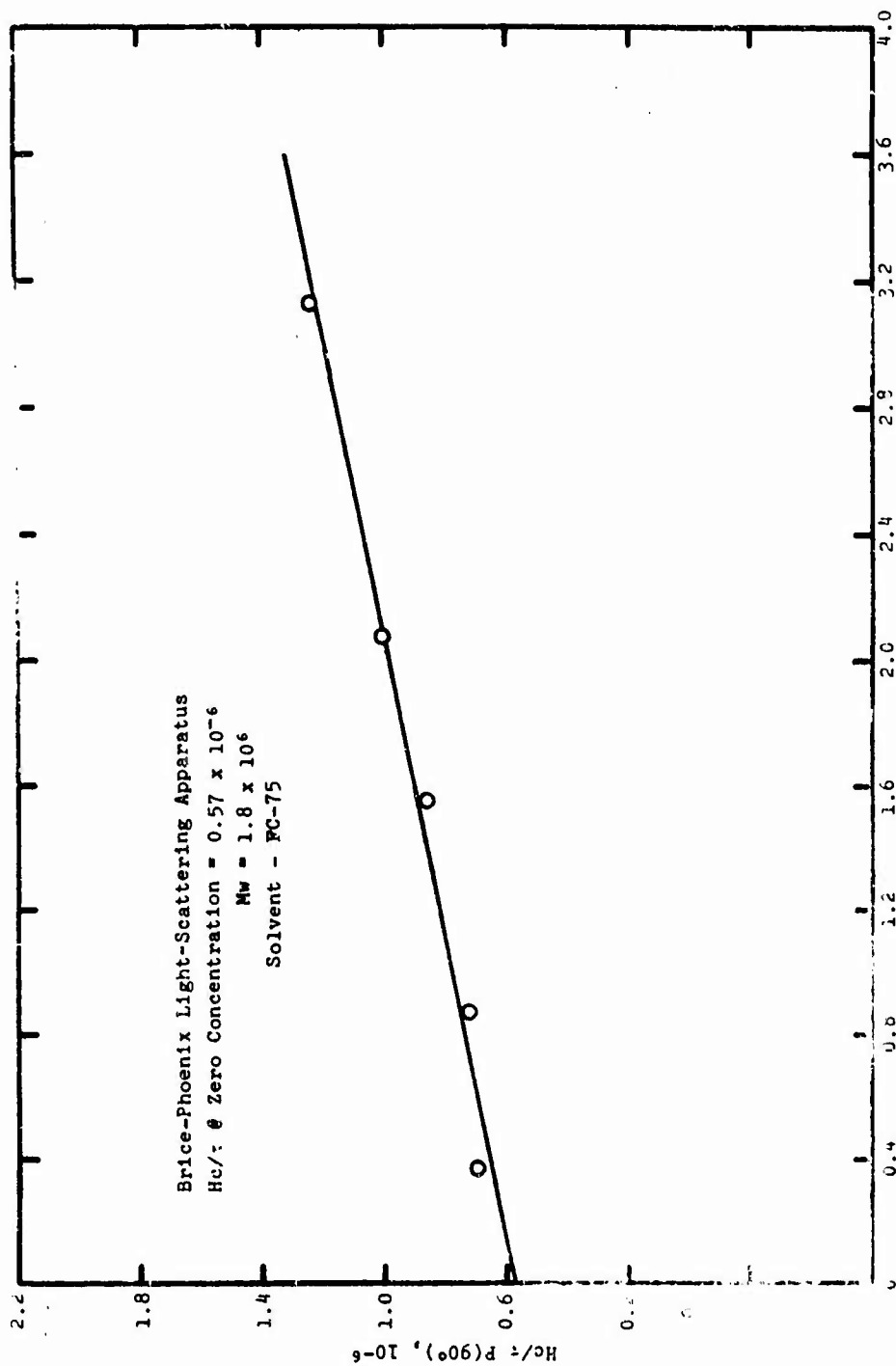


Figure 29. $H_c / P(90^\circ)$ Versus Concentration for the CF_3NO/C_2F_4 Copolymer Fraction No. 4, Run No. 2, Thiokol Sample XP5702.

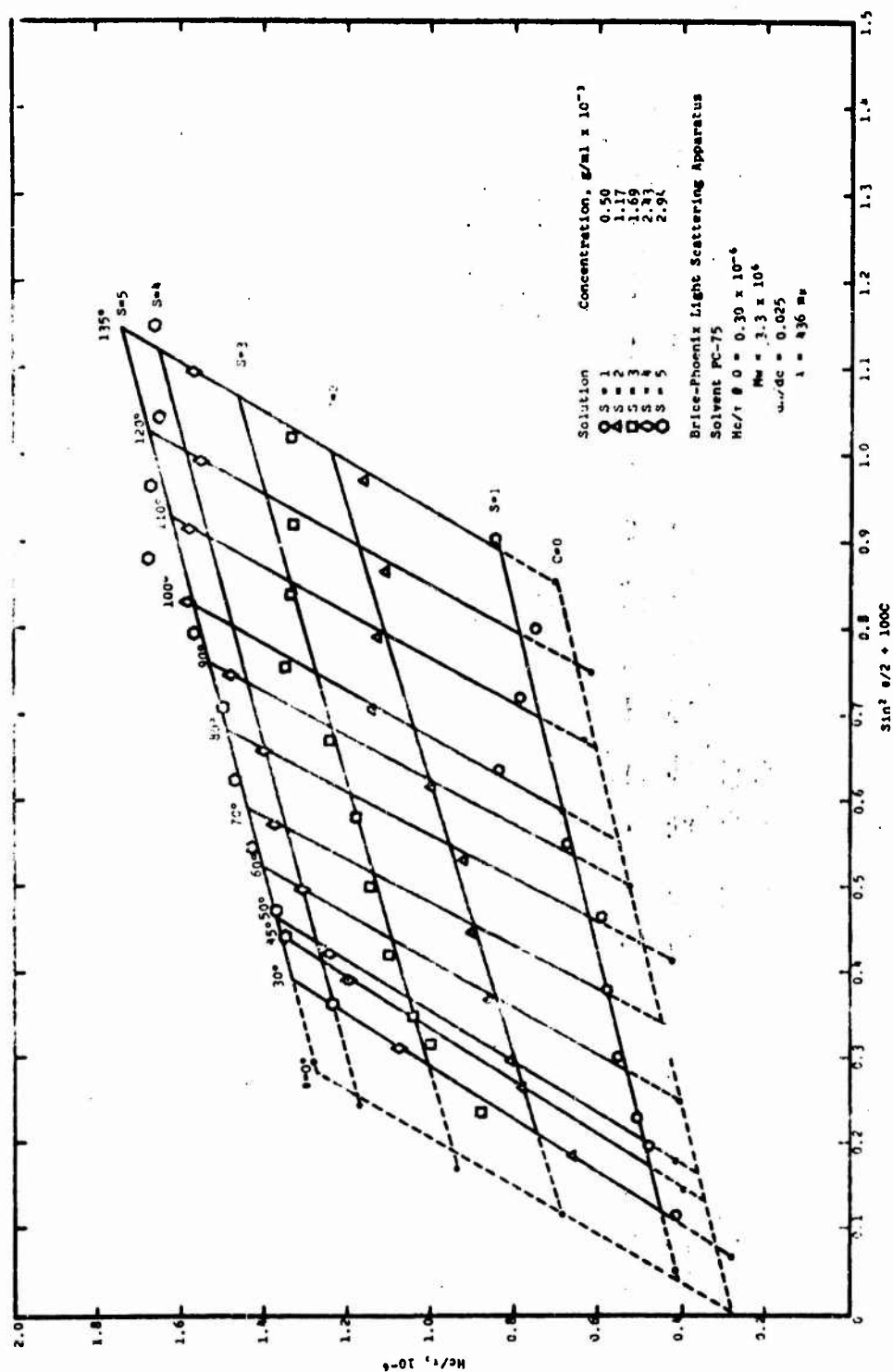


Figure 30. Zimm Plot of $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymer Fractions No. 13 and 14, Run No. 3, Thiokol Sample XP5702.

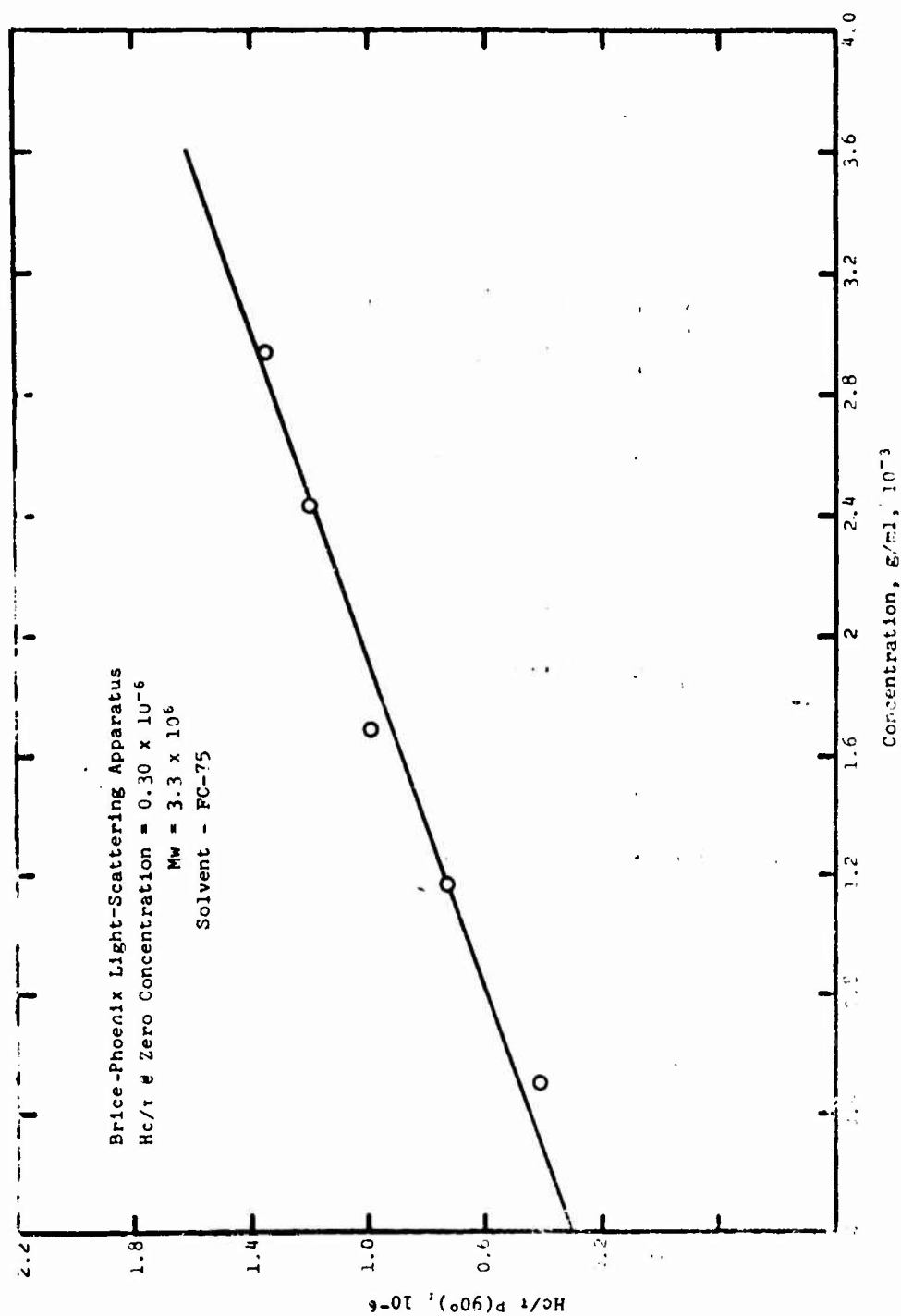


Figure 31. $H_c/\tau P(90^\circ)$ Versus Concentration For The CF_3NO/C_2F_4 Copolymer, Fractions No. 13 and 14, Run No. 3, Thiokol Sample XF5702.

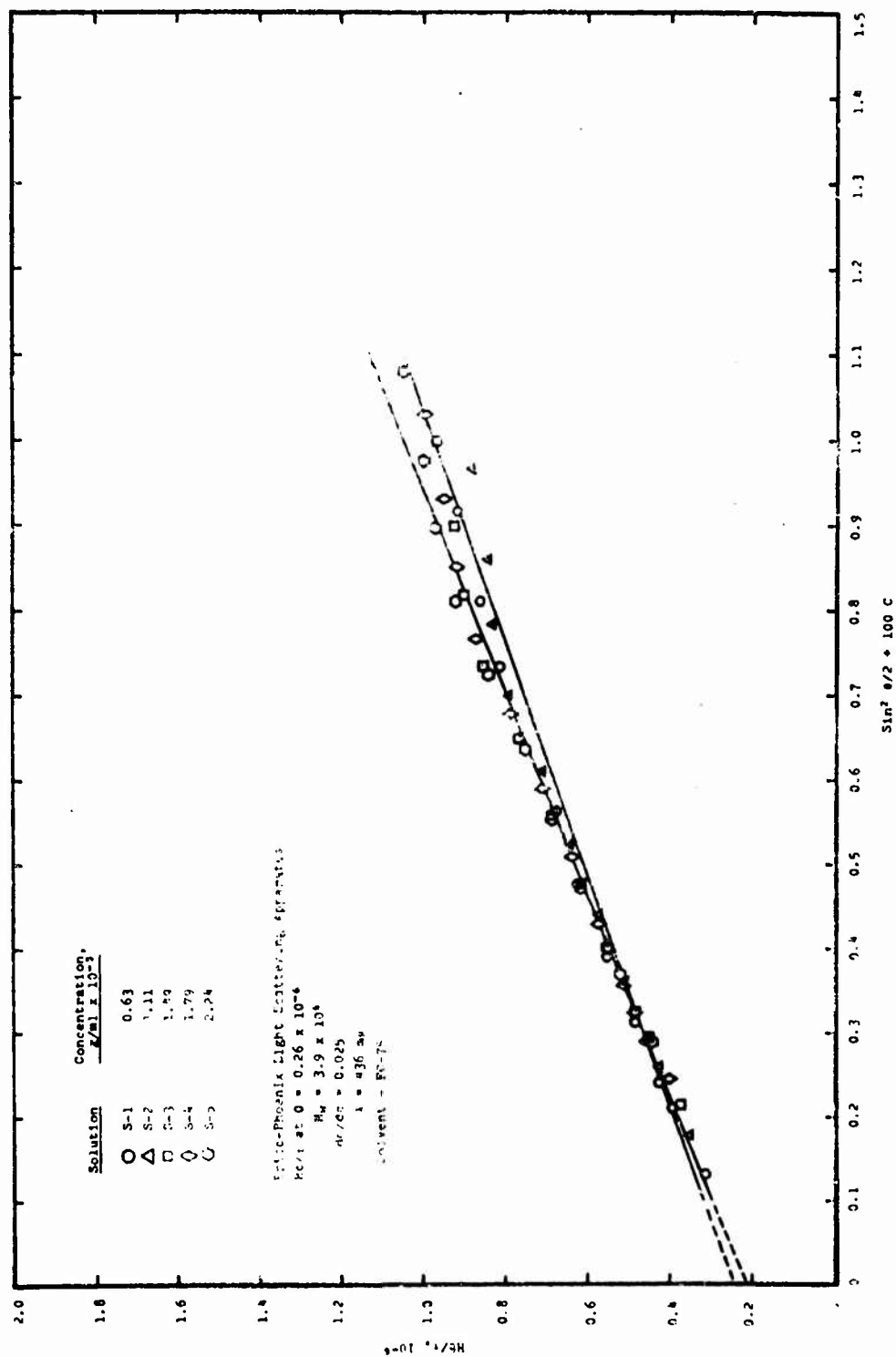


Figure 32. Zimm Plot of CF_3NO/C_2F_4 Copolymer, Fraction No. 15, Run No. 3, Thiokol Sample XP5702.

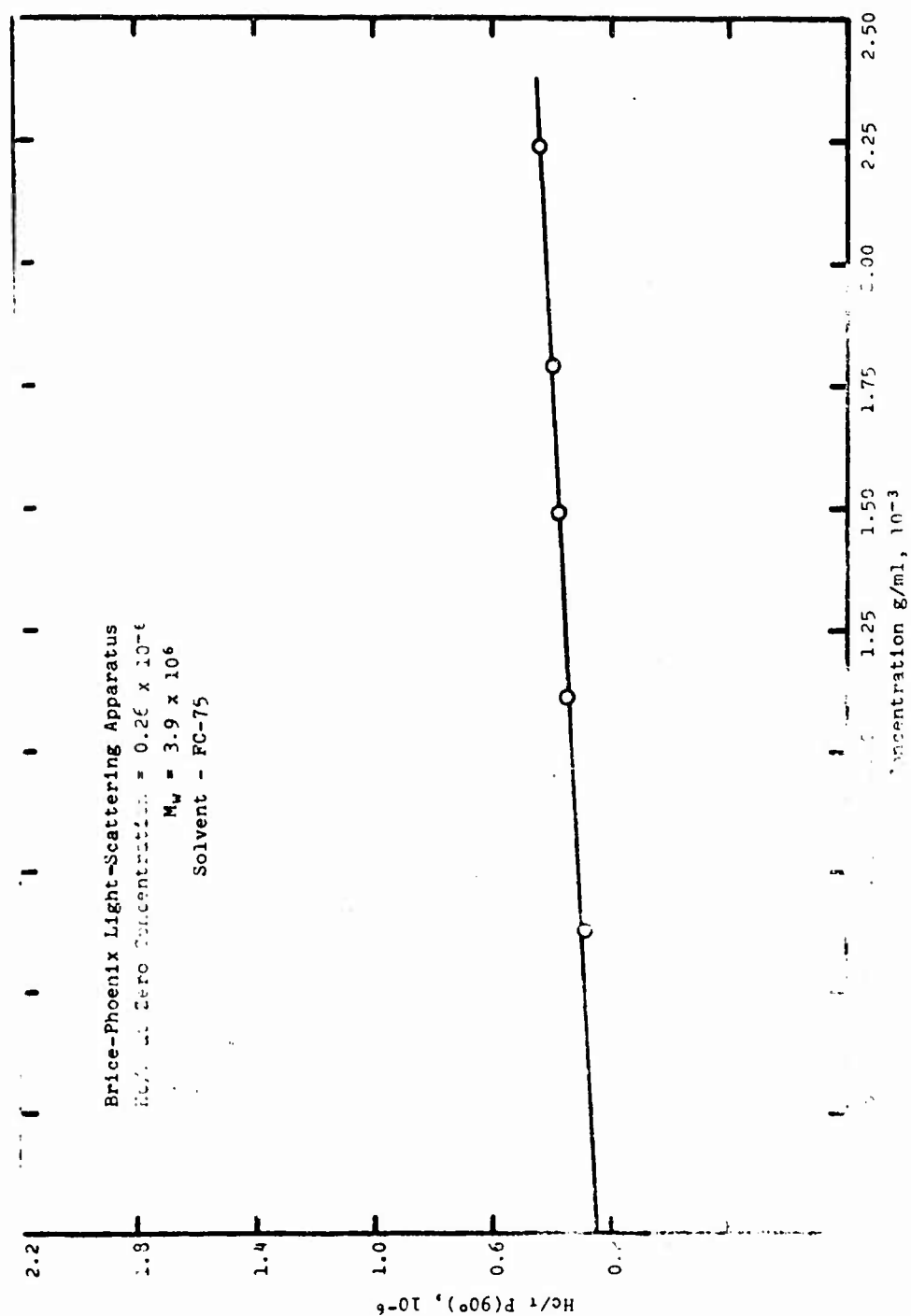


Figure 10. $H_0/\tau P(90^\circ)$ Versus Concentration for the CF_3NO/C_2F_4 Copolymer, Fraction No. 15, Run No. 3, Thiokol Sample XP5702.

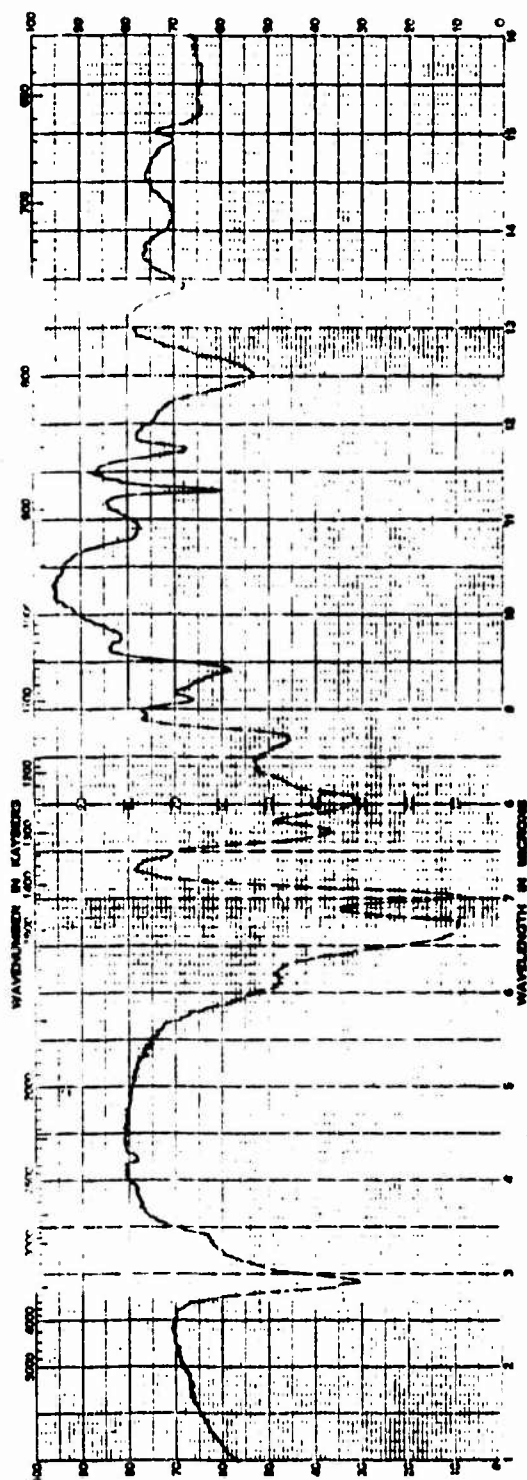


Figure 34. Infrared Spectra of White Precipitate From Thiokol CF₃NO/C₂F₄ Gum Sample XP5702.

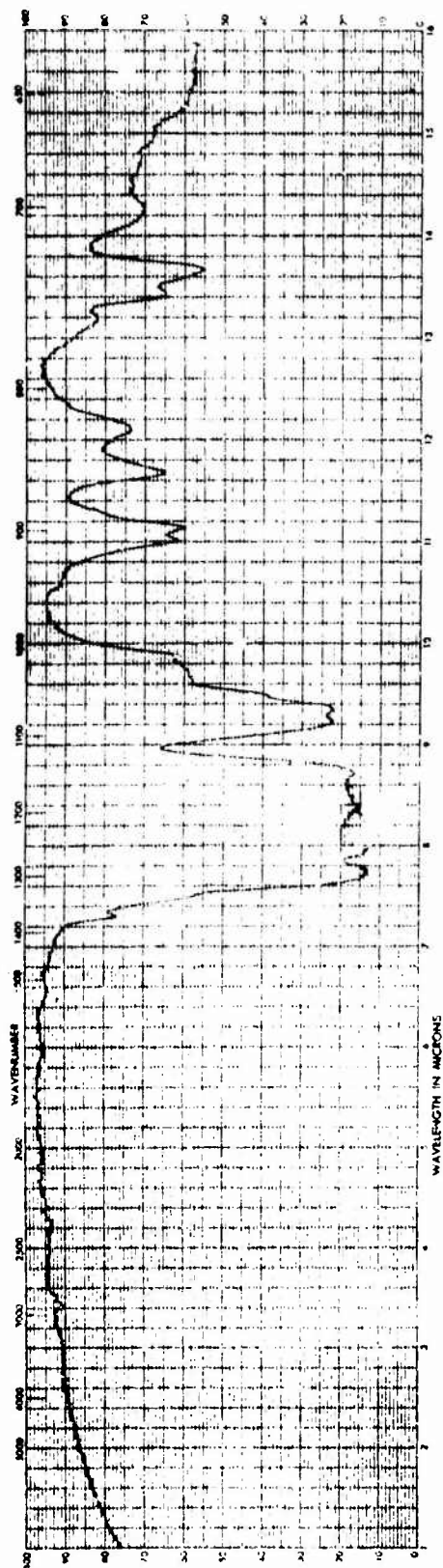


Figure 35. Infrared Spectra of Volatile Product From Thiokol $\text{CF}_3\text{NO/C}_2\text{F}_4$
Gum Sample XP5702.

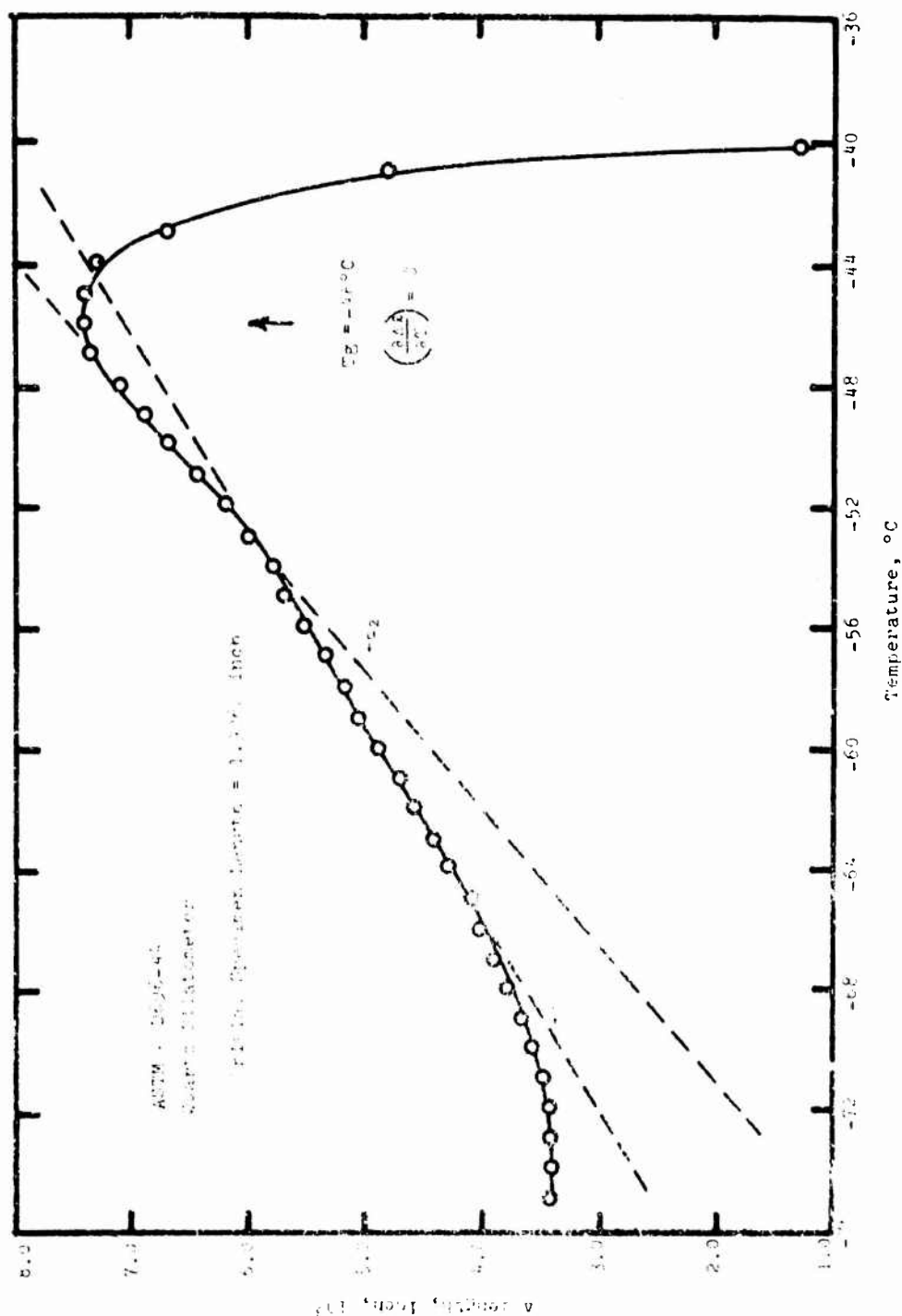
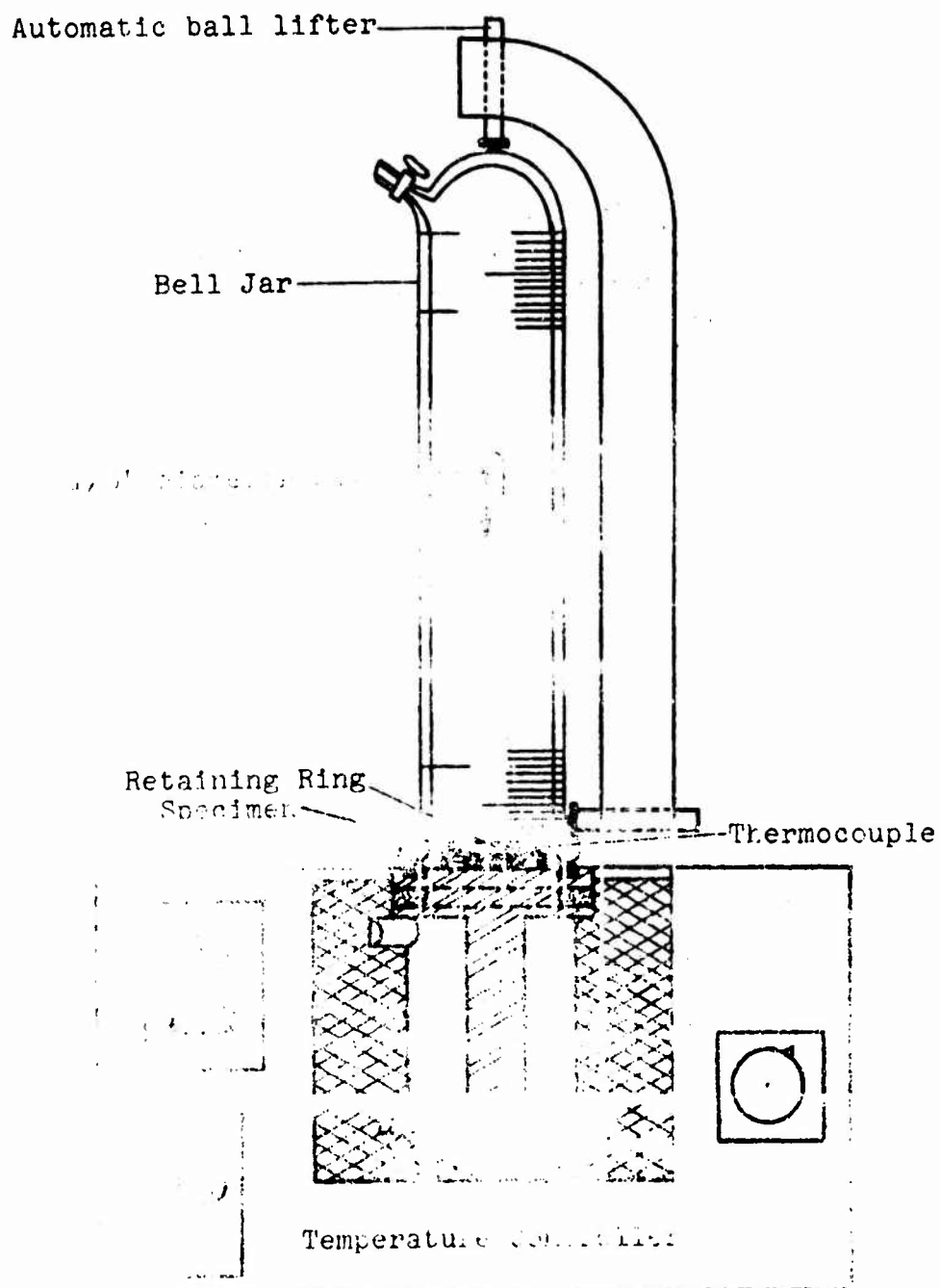


Figure 37. Thermal Expansion of $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Gum Sample XP5702.



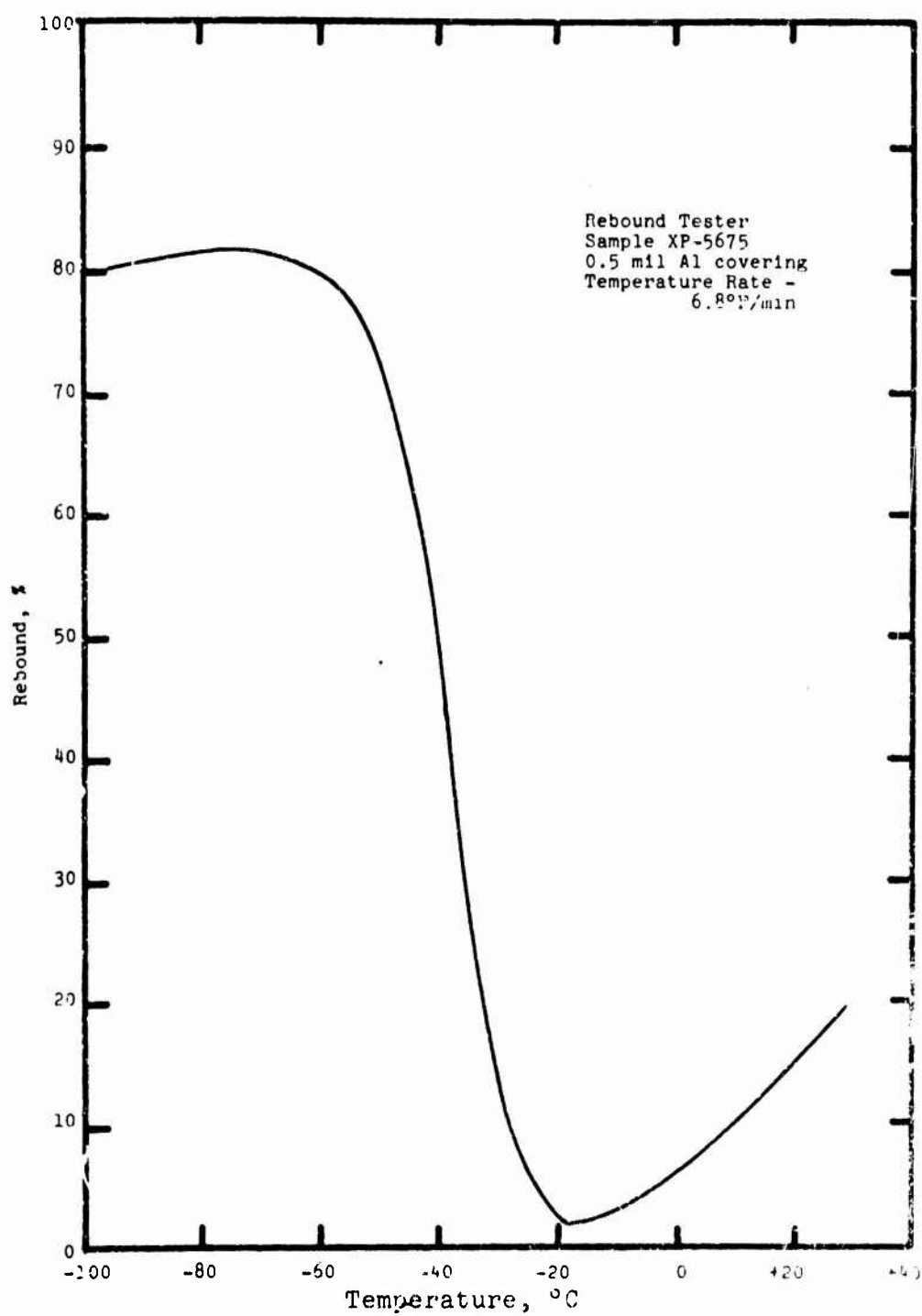


Figure 39. 1000 Cycles Per Second Modulus By Rebound Technique On $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Sample XP5675.

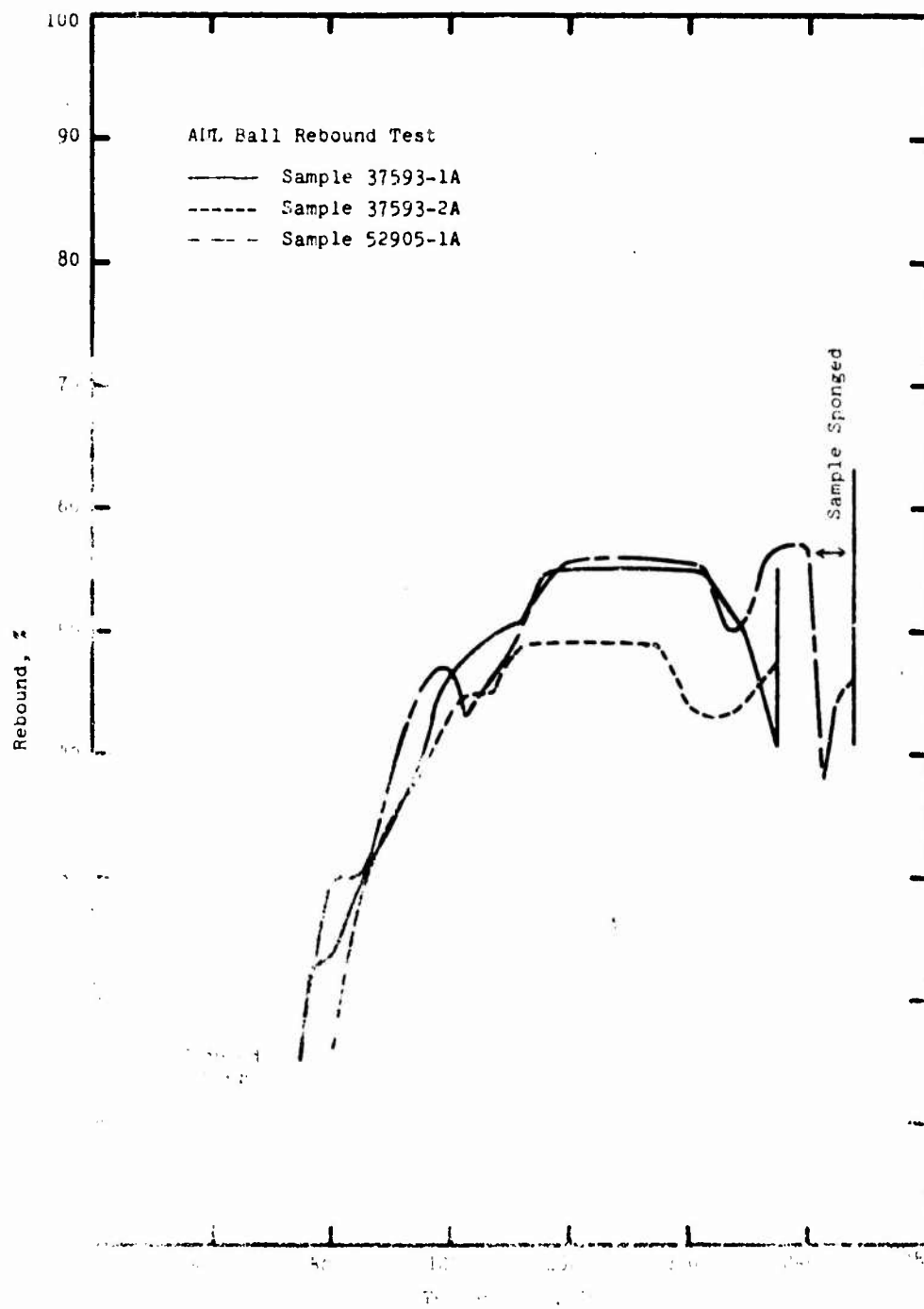


Figure 40. Amine-curing cycles of $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Gums Utilizing The 1000 Cycles Per Second Rebound Technique.

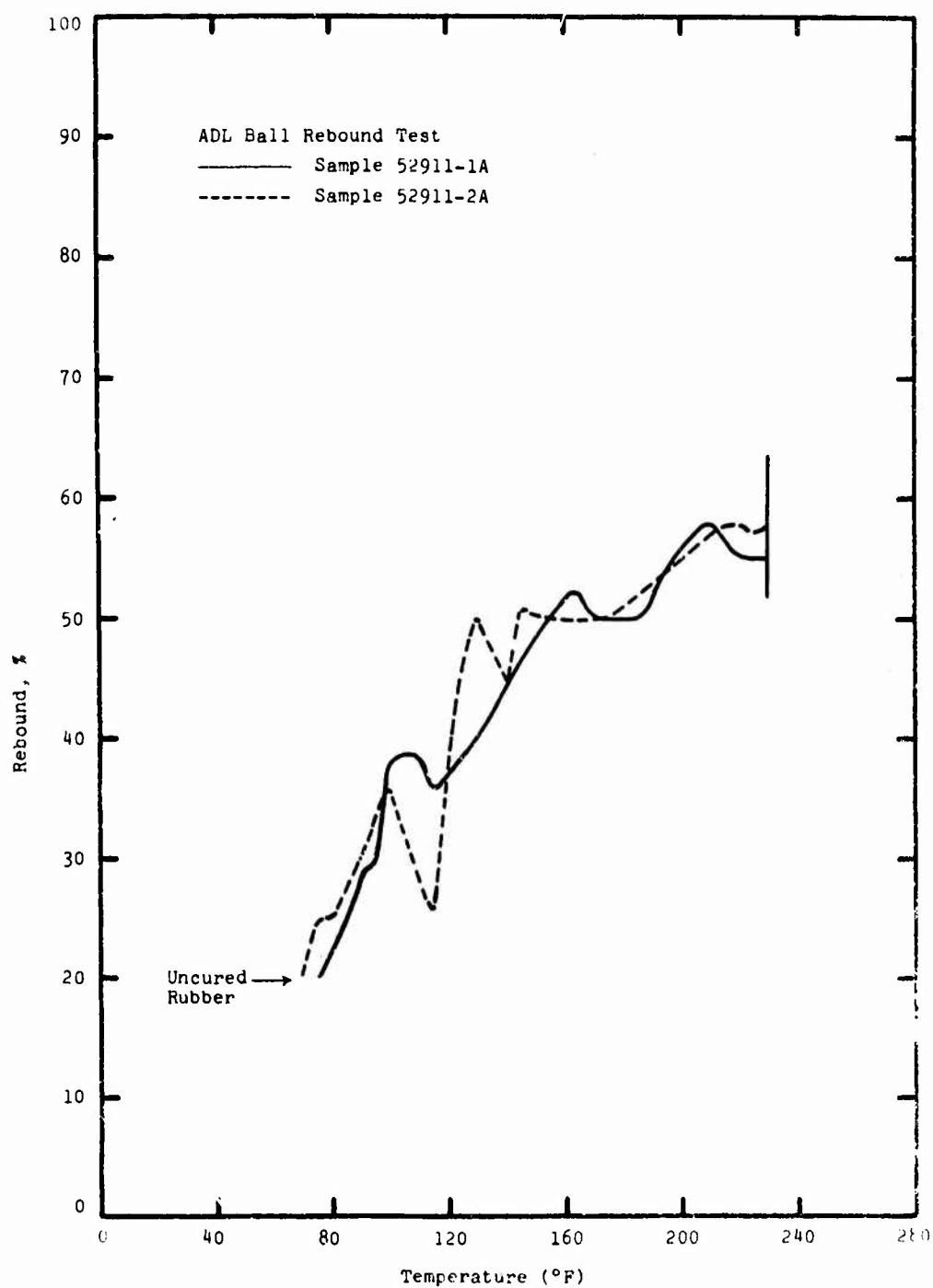


Figure 41. Amine-Curing Cycles of $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Gums Utilizing The 1000 Cycles Per Second Rebound Technique.

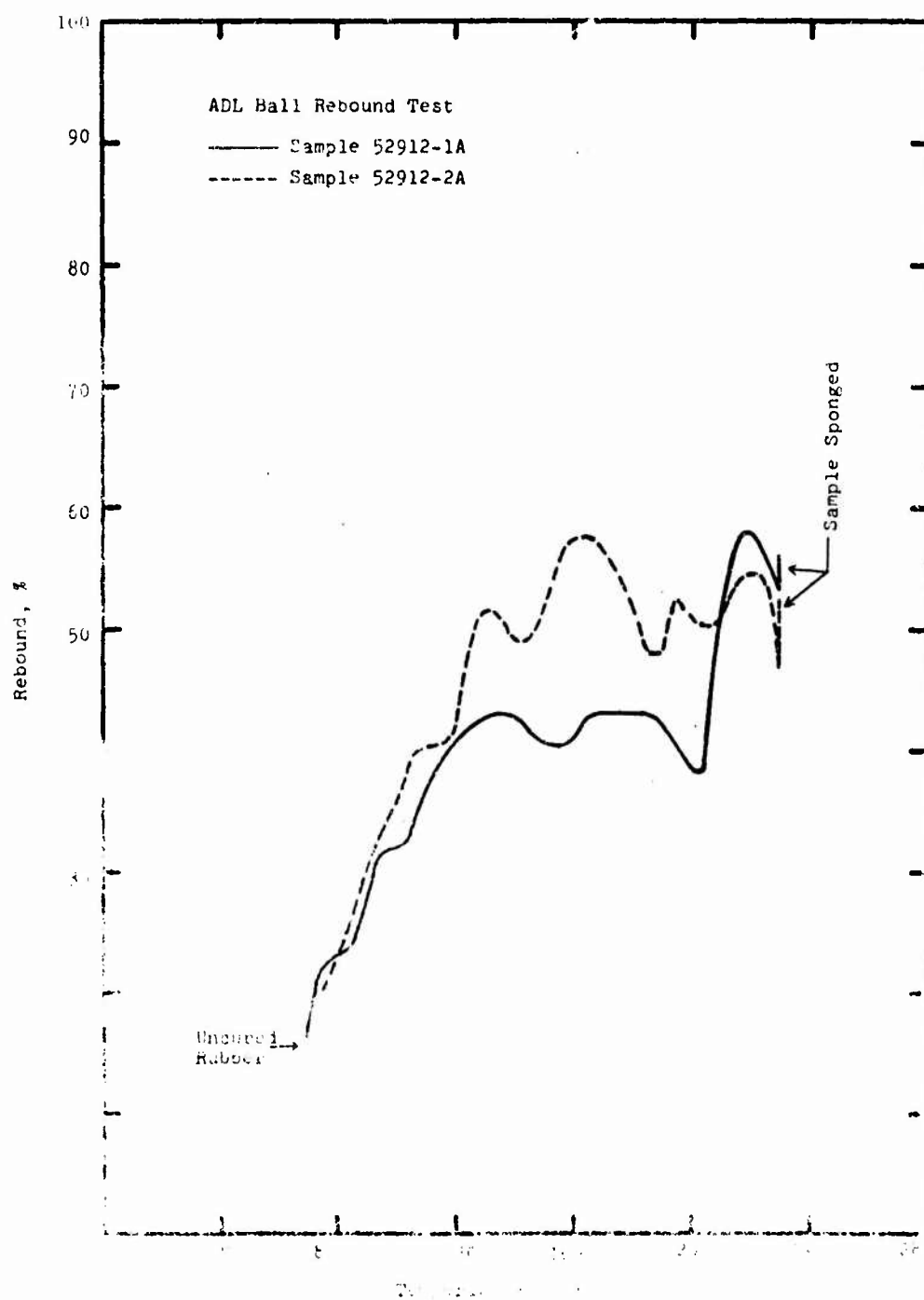


Figure 42. Amine-Curing Cycles of $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Gums Utilizing The 1000 Cycles Per Second Rebound Technique.

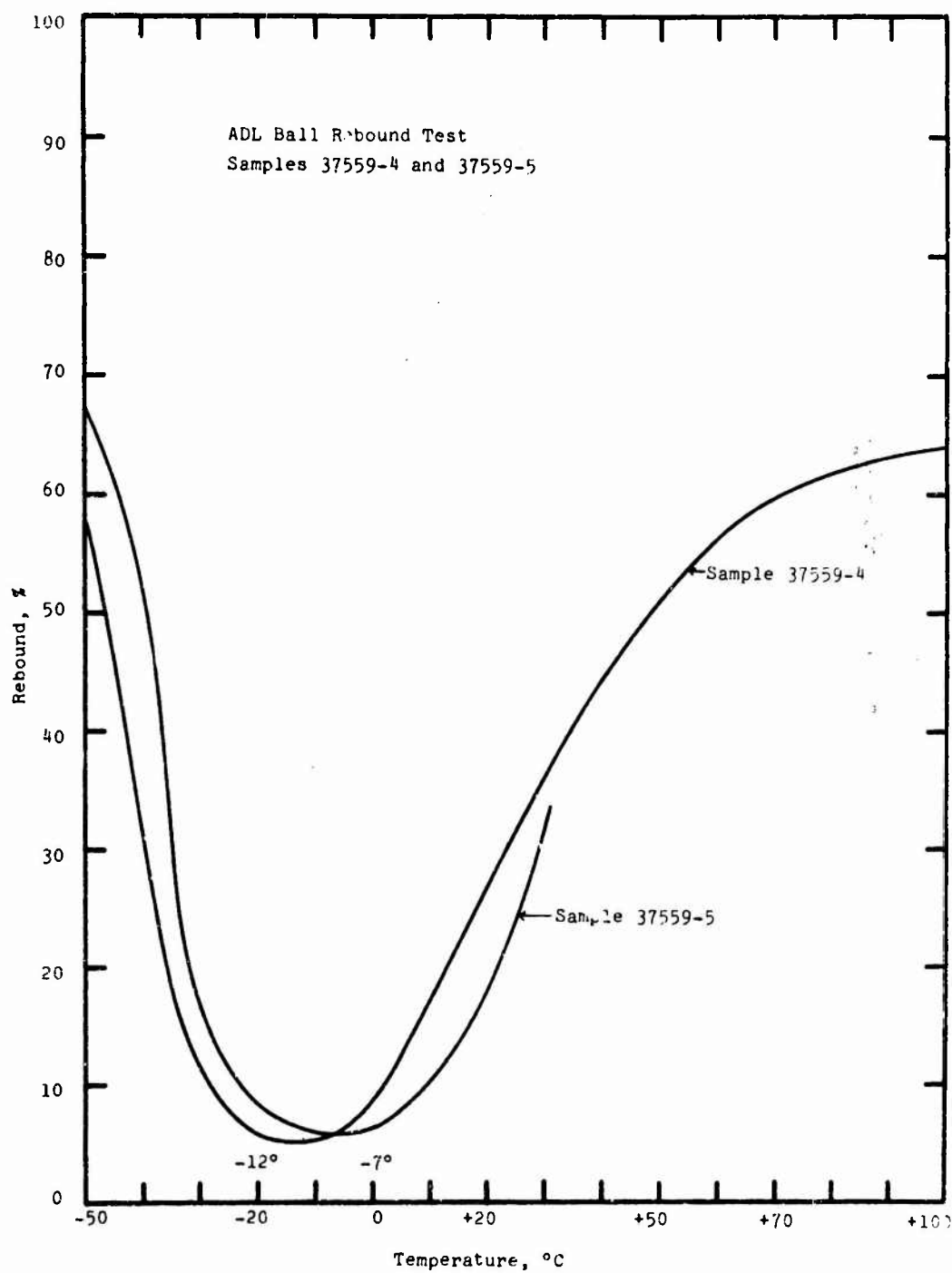


Figure 43. 1000 Cycles Per Second Modulus By Rebound Technique On $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Rubber Samples 37559-4 and 37559-5.

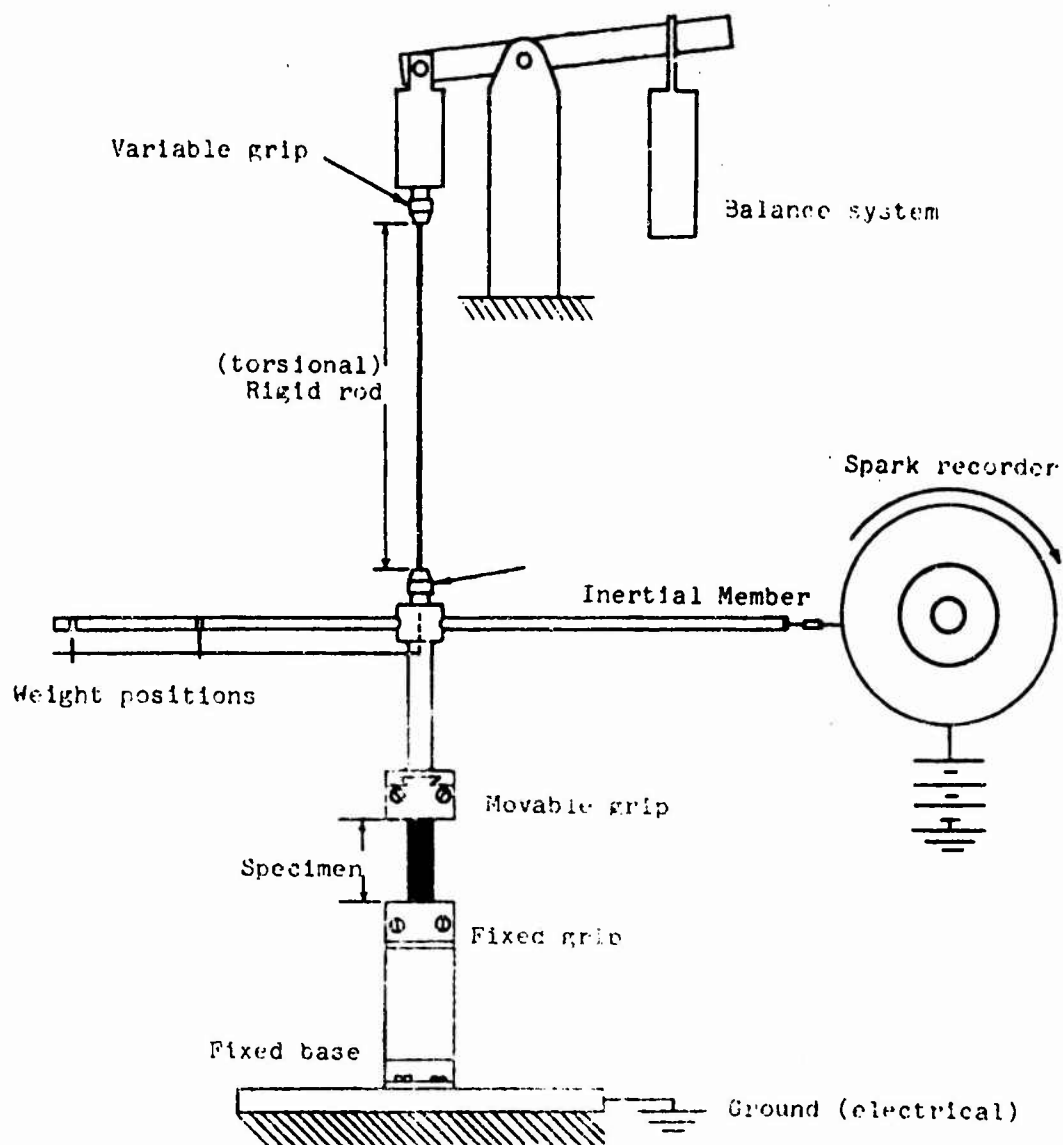


Figure 44. Modified Nonius Torsion Pendulum Apparatus For Determination of 3 cps Modulus.

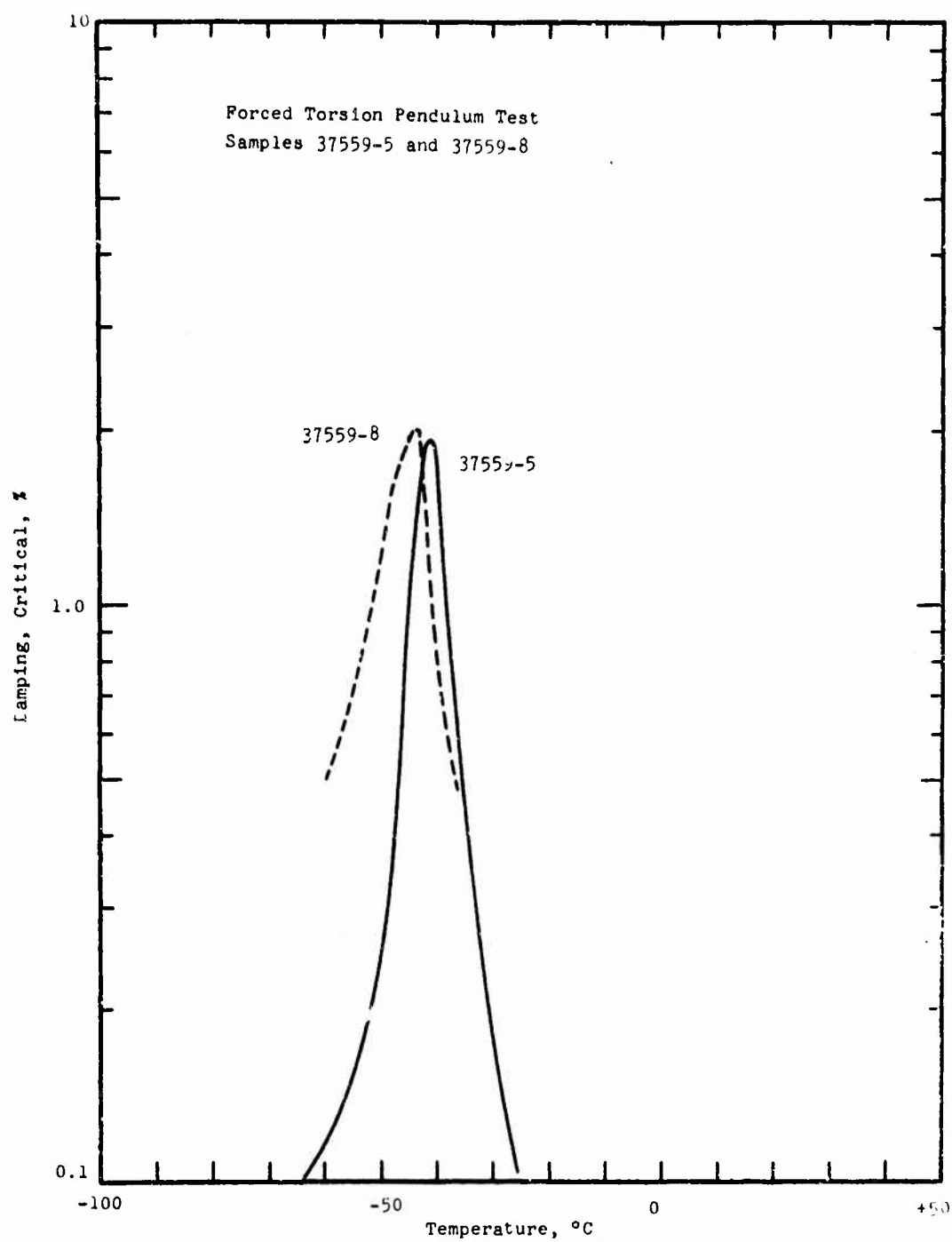


Figure 45. 3 cps Modulus By Modified Nonius Torsion Pendulum Technique of $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Rubber Samples 37559-5 and 37559-8.

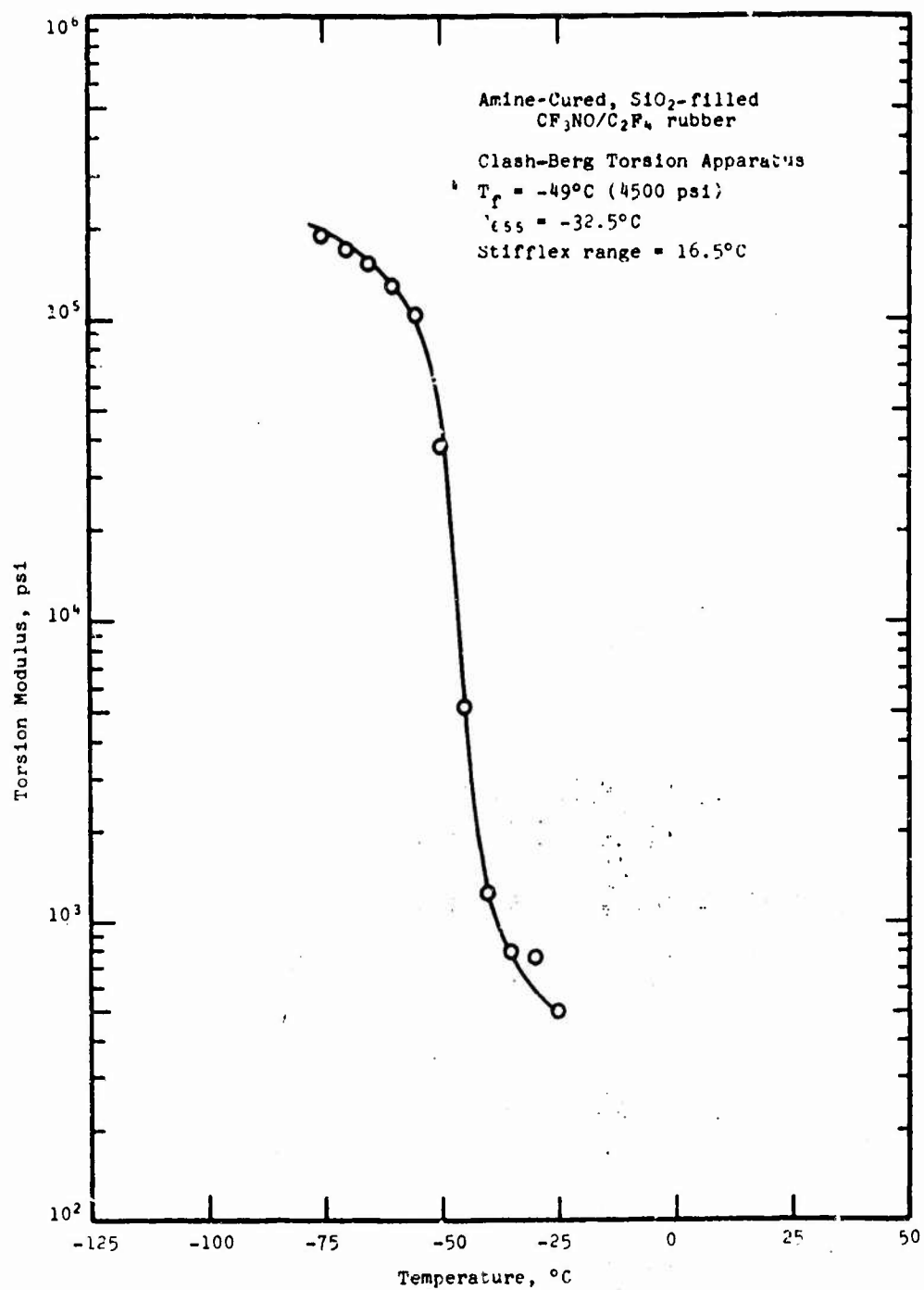


Figure 46. Clash-Berg Torsion Modulus of
CF₃NO/C₂F₄ Rubber Sample 37559-5.

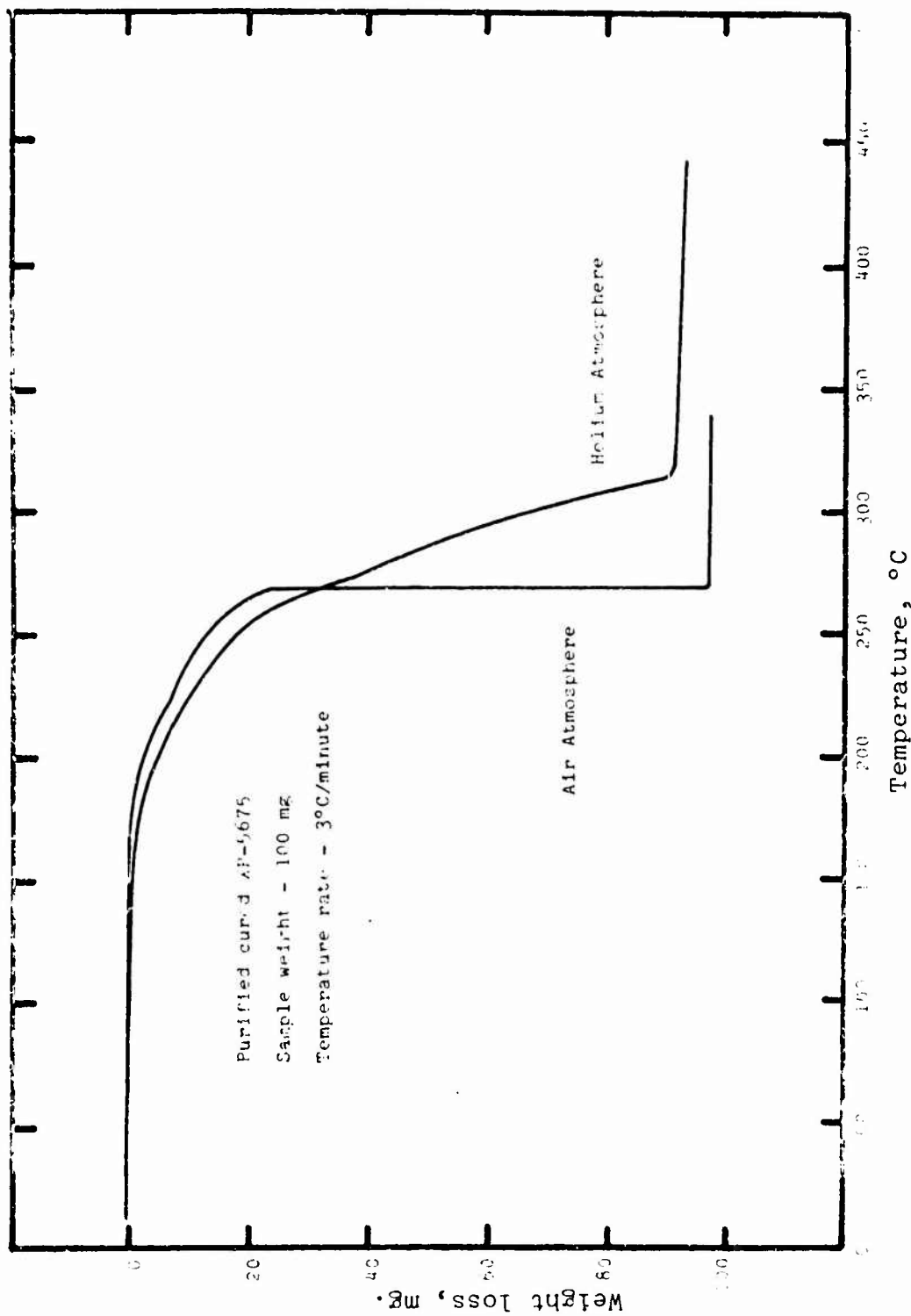


Figure 27. Thermogravimetric Analysis in Air and Helium of An Amine-Cured $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymer.

10.0

Temperature = 25°C

Data Points:

- 1 Thiokol Sample XP5702, fraction 4
- 2 Thiokol Sample XP5702, fractions 13, 14
- 3 Thiokol Sample XP5702, fraction 15

$\eta = 0.15 \times 10^{-3}$

$\eta = 0.15 \times 10^{-3}$

$\alpha = 0.7$

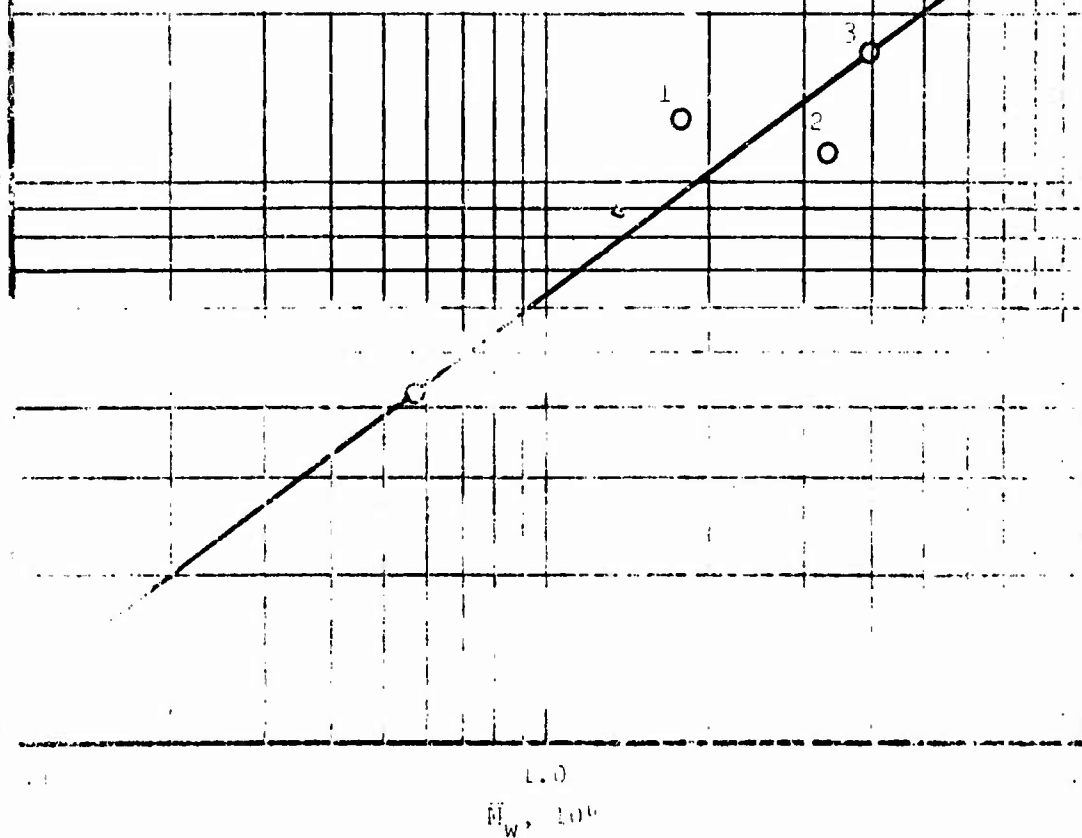


Figure 4b. Viscosity - Molecular Weight Relationship of CF_3NO/C_2F_6 (1:30-7 (factor of 10³ in viscosity) in ethers) at 25°C.

APPENDIX C

SOLUTION VISCOSITY MEASUREMENTS AND CLEANING PROBLEMS

1. General

The nitroso copolymers received had to be cleaned in order to remove gel particles and insoluble material. Between 20-40 gms of material were cleaned at one time. The material was placed in a quart bottle and 400-500 ml of FC-75 was added. The bottle was put on a tumbling wheel and left to tumble for two to four weeks. After this length of time, the material was finely divided, dispersed, and in solution as much as could be expected. The solution was then heated to 80°C in an attempt to produce further solution.

Problems existed in filtering. First, the solution was filtered through a stainless steel cloth (300 mesh). This removed the larger pieces of gel. It was then filtered by means of a suction flask using Whatman's filter paper #1. This did not seem to clear up the solution satisfactorily. Centrifuging was tried, but did not help; also, it would have been a little impractical for cleaning up larger samples. Filtering through Whatman's filter paper #1 under atmospheric pressure was then performed. This was rather time-consuming but necessary. The solution had to be filtered at least three to four times before the solution looked fairly clear. There was always a very slight haziness that could not be removed. The filter paper had to be changed frequently due to the fact that it clogged up during filtering. Each filter was rinsed down with FC-75 before being replaced with a new filter.

The final method of filtering consisted of putting the gum into solution by tumbling, filtering through 300 stainless steel mesh to remove any large amounts of gel, and then filtering through Whatman's filter paper #1 three to four times.

After the solution was filtered, the nonsolvent benzonitrile was added. About 450 ml of benzonitrile was added to 300 ml of solution. The beaker was then placed in a water bath at 50°C, the water bath being placed on top of a magnetic stirring hot plate. Cold air was blown over the beaker by means of a heat gun. The solution was stirred

continuously during evaporation. After the solvent was evaporated, the material was removed from the beaker, placed in a vacuum oven, and heated at 60°C for 12 hours. The material was then considered purified.

2. Gel

Attempts were made to clean up XP5702 by means of a soxhlet extractor. A 10 gm sample was deposited in a thimble and the thimble placed in a soxhlet extractor. 300 ml of FC-75 was added to the flask and refluxed for 48 hours. The material became swollen and jellylike, consequently clogging up the thimble, which allowed the FC-75 to run only over the top of the material in the thimble. This thimble was removed from the extractor, the excess of solvent was dried with passing cold air, and then placed in a vacuum oven for 12 hours at 60°C. Fifty-six percent of undissolved material remained in the thimble.

Another approach was attempted utilizing a soxhlet extractor. This time a 10 gm sample was placed in a piece of stainless steel mesh (300 mesh) and placed in the thimble. After refluxing the FC-75, the material became swollen and jellylike and overflowed in the thimble, consequently clogging the extractor.

Similar problems existed when running viscosities. Unless the material was cleaned beforehand, there was always the problem of gel being present. In the case of PCR-bulk polymerization and solution-polymerization gums, intrinsic viscosities were measured without cleaning. Again gel was present in which case the gel had to be filtered through a stainless steel mesh (500) filter with new solvent. The concentration was determined on the clear portion. On the 10th of the month, PCR-bulk polymerization (fractions 13, 14, 15, 16), were present in the solutions, which made it impossible to determine viscosities. Concentrations of these solutions had to be redetermined by using the clear portion of the solutions.

A solution in FC-75 was made up of 11 gm of material, (FC-75) to determine the gel content. The solution was placed in a sampling wheel. The solution was filtered through a glass crucible, but the crucible clogged up shortly after the filtering began. Two cc of the

unfiltered solution was removed and placed in a two-ounce french square bottle; 10 cc of FC-75 was added. This was mixed well and then filtered through a weighed piece of Whatman's filter paper #1 until the solution was clear. The filter paper was dried at 60°C in a vacuum oven overnight and weighed. Recovery of 14.3% and at times as high as 45% gel was made.

3. Viscosity Measurement

Specific viscosities were determined in a Cannon-Fenske-Ostwald-type viscometer. The charge or loading capacity was approximately 7 ml.

Ordinarily, the viscometer would be filled by immersing the measuring side of the viscometer under the surface of the liquid and applying a gentle vacuum to the other end, completely filling the measuring side of the viscometer. The vacuum would be released, allowing the solution to drain back through the capillary until the meniscus reached the upper etch mark on the working capillary. Then the viscometer would be inverted to an upright position.

This technique could not be applied when running viscosities on the nitroso gum or copolymers, using FC-75 or FC-43, because of the low surface tensions. When trying to fill the viscometer in the above manner, difficulties were encountered in letting the solution drain back through the capillary. The solution would bubble and flow out of the viscometer rapidly so that too much of the solution was lost.

Consequently, the viscometer was loaded by means of pipettes. Seven ml were used to run the efflux time of the solvent, and 7 ml were used to determine the efflux time of the solution. The capacity of the viscometer was about 7 ml, so this enabled one to control the volume in both cases, thus providing precise measurements.

A three-way pipette manipulator was used to fill the pipettes, and a piece of tygon tubing about 1-inch long was melted onto a piece of stainless steel cloth (500 mesh) and was fitted over the delivery end of the pipette. This apparatus was used as a filter. The viscometer was filled and measurements were made both on solvent and solution. General practice was used for cleaning the viscometer.

When a sufficient amount of material was available, a 0.1% solution was made using 0.05 gm of gum to 50 ml of solvent. It was impossible to follow this practice when working with the samples collected from the fractionation technique. The amount of sample available was used and the volume of the solvent was adjusted in order to have a 0.1% solution. In a few cases, a 0.1% solution could not be obtained and smaller concentrations such as .05% were utilized.

APPENDIX D.

FRACTIONATION PROCEDURES

Several techniques were tried for fractionating and the one used shall be discussed. This method was used both in the fractionation of XP5702 runs 3 and 4, and the PCR-bulk-polymerization gum. Sample XP5702 was purified, as mentioned in the cleaning procedure (Appendix C), and the PCR was assumed purified when received.

The conditions for fractionating were the same for both samples. The elution technique method was used (Ref. 4).

A 1.5 gm sample was weighed and deposited in a two-ounce french square bottle. The polymer was put into solution by adding 29 ml of FC-75 and heating to 80°C. After the polymer was in solution, 21 ml of benzotrifluoride was added to the hot solution and reheated so the material could go back into solution. The solvent/nonsolvent system used above was based on prior determinations (see Section K). Under these conditions, the polymer was all in solution at 80°C and precipitated at 25°C. The solution was ready for deposition.

The elution column consisted of cleaned, pure silica sand of from -40 to +200 mesh particle size. N₂ gas was used as a back pressure to regulate the flow of the solvent over the sand. The column was maintained at 78°C by refluxing ethanol in the jacket. The solution at 80°C was poured on the column and allowed to elute 2/3 of the way down the sand. After the solution was added, the column was cooled slowly in order to cause selective deposition of the polymer. Nitrogen was left to flow through the column for 48 hours to dry the column.

After the column was dry, 200 ml of benzotrifluoride was flushed through the column to set the polymer to the substrate.

Fractionation was then begun. First the ethanol jacketing solvent was removed and replaced with acetone. The column was heated with acetone, refluxing in the jacket at 56°C.

Removal of the polymer fractions was performed by eluting with solvent/nonsolvent mixtures of FC-75 and benzotrifluoride. Progressive elutions were then performed by solvent/nonsolvent mixtures, enriching with solvent and decreasing with the nonsolvent as follows.

	<u>Solvent, FC-75</u>	<u>Nonsolvent, Benzotrifluoride</u>
Fr 1	35	65
Fr 2	38	62
Fr 3	41	59
Fr 4	42	58
Fr 5	43	57
Fr 6	44	56
Fr 7	45	55
Fr 8	46	54
Fr 9	47	53
Fr 10	48	52
Fr 11	49	51
Fr 12	50	50
Fr 13	51	49
Fr 14	55	45
Fr 15	60	40
Fr 16	100	0

The fractions were recovered in weighed beakers and evaporated to dryness at 50°C. The fractions were then dried in a vacuum oven at 60°C for 24 hours, desiccated, then weighed again to determine the amount of each fraction recovered.

A specific viscosity was then measured in FC-75 at 25°C.

Intrinsic viscosities were calculated from the specific viscosities by the Huggins' equation,

$$K'c[\eta] + [\eta]^2 - \frac{\eta_{sp}}{c} = 0$$

The molecular weight was calculated using the intrinsic viscosities and the Mark-Houwink equation,

$$[\eta] = K(M_W)^a$$

where $K = 3.171 \times 10^{-5}$, and $a = .717$.

The summation percent of the fractions was calculated and the integral and differential molecular distribution curves were plotted.

C_i = percent i'th fraction is of the composition.

M_i = molecular weight of i'th fraction.

M_N = number average molecular weight.

M_W = weight average molecular weight.

$N_i = C_i/M_i$

$\Sigma \text{ wt. \% or } \Sigma\% = \text{summation weight percent.}$

and M_N was calculated from: $M_N = \frac{100}{\Sigma C_i/M_i}$

APPENDIX E.

LIGHT-SCATTERING PROCEDURE

A K value for the Differential Refractometer was determined. This value is used for measuring the dn/dc value for light-scattering.

A constant, a , which is used in the turbidity equations for light-scattering had to be determined. This is an instrumental constant relating the working standard to the reference standard opal glass.

A calibration factor known as r/r' was determined. This is a factor relating the narrow beam geometry to the standard beam geometry when using a cylindrical cell. This factor also is used in the turbidity equation.

The quantity $(n - n_0/C)$ is a constant (refractive increment) for a given solute-solvent system, and was determined by the Brice-Phoenix Differential Refractometer.

An NBS Standard polystyrene sample was checked. Therefore, r/r' was again measured since the factor is dependent for each solute-solvent system to be studied. Also, $(n - n_0/C)$ was measured because of the different solute-solvent system used: dn/dc at 546 μ for polystyrene = 0.1097, refractive index = 1.497 at 546 μ .

The light-scattering data were collected on a cylindrical cell at 436 μ wavelength and 25°C. The cylindrical cell was used in order to measure the scattering at angles from 135° to 30°. From this data, a Zimm plot was drawn. Wavelength 436 μ was used instead of 546 μ , because sufficient scattering was not obtainable at 546 μ , resulting in low galvanometer deflections and poor accuracy.

The cylindrical cell used was scrupulously cleaned, inside and outside, with detergent solutions before use. After cleaning, the cell was rinsed with distilled water, triple distilled water, and finally with distilled methanol.

Pipettes used for transferring were immersed in cleaning solution at least 24 hours, rinsed with tap water, distilled water, triple distilled water, and distilled methanol, then dried.

Solvent and solutions were filtered through millipore filters plus a millipore filtering funnel enclosed in a pressurized chamber. (Nitrogen was used to filter solutions and solvent.) A 0.45 μ millipore filter was used for solutions and 100 μ millipore filter was used for the solvents.

The solvent was filtered a minimum of three times directly into the clean cylindrical cell, washing the inside walls down each time with the solvent. Adequate cleaning was important in order to yield accurate molecular weights. A stock solution was also filtered until the solution was perfectly clear, then filtered into a scrupulously clean bottle until ready for use. The solution was filtered first and then when ready for the test, the solvent was filtered, as described above, in the cell. Thirty ml of solvent was required for the cell. Scattering was measured on the solvent and then different amounts of stock solution were added to the solvent, with the scattering measured on each concentration respectively. Five concentrations were run.

The data were then ready for calculations. The apparent turbidities were calculated for each concentration and for the solvent. The data were computed on an IBM 702 computer and plotted by hand.

dn/dc used for nitroso copolymers = 0.025 at 436 μ
Refractive index at 436 μ = 1.281

APPENDIX F.

DETAILS OF FORMULATION, CURING, AND PHYSICAL TESTING OF THE $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ RUBBER

Eleven "Master Batches" were prepared, nine of which contained $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ gum XP5887, one of which contained "purified" gum XP5702, and one which contained Peninsular ChemResearch "purified" bulk polymerized gum. These "Master Batches" were prepared on a two roll rubber mill and stored in a freezer to prevent initial curing before the molding procedure.

The test samples were prepared from the "Master Batches" in two steps - molding and postcuring.

1. Molding Procedures

A. Sample # 37593-1 cure #1

- a. 7.5 grams of the "Master Batch" were placed in a 2" dia. x 60 mil shim mold between two sheets of teflon.
- b. The press was preheated to 120°C.
- c. The mold was placed on the press and the press faces were brought together (no pressure applied) for 5 minutes.
- d. 1000 lb (gage) pressure was applied and the press was pumped four to five times.
- e. The mold was left in the press at 120°C and 1000 lb (gage) pressure for 3 hours.

B. Samples - 37593-1 cure #2 to cure #4; 37593-2 cure #1 to cure #3; 37593-3 cure #1 to cure #2; 37593-4 cure #1 to cure #3; 37593-5 cure #1 & #2.

- a. 7.5 grams of "Master Batch" were placed in a 2" dia. x 60 mil shim mold between

two sheets of Teflon. (33 grams used in a 4" x 4" x 60 mil shim mold for 37593-2 cure #3).

- b. The press was preheated to 100°C.
- c. The mold was placed on the press and the press faces were brought together (no pressure applied) for 5 minutes.
- d. 1000 lb (gage) pressure was applied and the press was bumped four to five times.
- e. The mold was left in the press at 100°C and 1000 lb (gage) pressure for 1 hour.

C. Samples - 37593-1 cure #5; 37593-2 cure #4; 52911-1 cure #1; 52911-2 cure #1

- a. 7.5 grams of the "Master Batch" were placed in a 2" dia. x 60 mil shim mold between two sheets of Teflon.
- b. The mold was placed on the press and the press faces were brought together (no pressure applied) at room temperature.
- c. The temperature was increased to 55°C and held.
- d. After 5 minutes at 55°C, 1000 lb (gage) pressure was added and the press was bumped four to five times.
- e. The mold was held at 55°C and 1000 lb (gage) pressure for 1 hour.

D. Samples - 37593-1 cure #6; 37593-2 cure #5; 52912-1 cure #1; 52912-2 cure #1

- a. 7.5 grams of "Master Batch" were placed in a 2" dia. x 60 mil shim mold between two sheets of Teflon.

- b. The mold was placed on the press and the press faces were brought together (no pressure applied) at room temperature.
 - c. The temperature was increased to 55°C and 1000 lb (gage) pressure was applied. The press was bumped four to five times and the mold was held at 55°C and 1000 lb (gage) pressure for 15 minutes.
 - d. The temperature was raised to 75°C and held for 15 minutes (still at 1000 lb (gage) pressure).
 - e. The temperature was increased to 100°C and held for 30 minutes (pressure still at 1000 lb (gage)).
- E. Samples - 37593-3 cure #3; 52905-1 cure #1; 52905-2 cure #1
- a. 7.5 grams of the "Master Batch" were placed in a 2" dia. x 60 mil shim mold between two sheets of Teflon.
 - b. The press was preheated to 100°C.
 - c. The mold was placed on the press and the press faces were brought together (no pressure applied).
 - d. After 5 minutes in the press, 250 lb (gage) pressure was applied for 1 minute. The press was bumped four to five times (temperature held at 100°C).
 - e. The pressure was increased to 500 lb (gage) pressure one minute. The press was bumped four to five times (temperature held at 100°C).
 - f. The pressure was increased to 750 lb (gage) for 1 minute. The press was bumped four to five times (temperature held at 100°C).
 - g. The pressure was increased to 1000 lb (gage) and held for 1 hour. The press was bumped four to five times (temperature held at 100°C).

Of the five procedures, "D" and "E" appeared to give the best results. Procedure "A" gave irregular surfaces to the sample (temperature too high, above curing range). Procedure "B" was good, however; stepping the temperature appeared to be better. Procedure "C" gave irregular surfaces to the sample (temperature was not high enough to allow the rubber to flow properly and initiate cure).

2. Postcuring and Durometer A-2 Readings

After molding, the samples were postcured in an oven over a period of about 24 hours. Postcuring stages and Durometer (Shore A-2) readings corresponding to each sample at each stage of postcuring are as follows:

A. Sample No. 37593-1 cure #1

Postcure: Time (hrs)/Temp (°F) 16/122, 3/158, 5/185, 17/203, 5/212

Shore A-2 readings:

Before	158°F		185°F		203°F		212°F		
Postcure	1-1/2 hr	3 hr	2-1/2 hr	5 hr	16 hr	17 hr	2-1/2 hr	5 hr	Final
	40	43	43	44	44	47	48	49	49

B. Samples No. 37593-1 cure #2, 37593-2, cure #1, 37593-4 cure #1, 37593-5 cure #1

Postcure: Time (hrs)/Temp (°F) 1/122, 1/167, 1/212, 16/230, 2-1/2 /257

Shore A-2 readings:

Sample No.	Before P.C.	122°F		167°F		212°F		257°F		230°F		257°F		Final
		1/2 hr.	1 hr	1/2 hr	1 hr	1/2 hr	1 hr	1/2 hr	1 hr	16 hr --	1 hr	1 1/2 hr		
37593-1 cure #2	40	40	40	40	41	41	41	35	31	31	--	31	41	31
37593-2 cure #1	47	48	48	48	49	50	52	57	57	63	--	64	64	64
37593-4 cure #1	30	33	34	34	35	36	37	36	34	39	--	41	41	41
37593-5 cure #1	28	31	33	34	35	36	37	32	30	37	--	39	39	39

NOTE: During the postcure of the above samples, all but sample 37593-2 cure #1 began to sponge (show gas) when the temperature of the oven was increased from 212°F to 257°F. This led to the belief, that the temperature range between 212°F and 230°F was critical for these specific nitroso samples.

C. Samples No. 37593-1 cure #4, 37593-2 cure #3, 37593-3 cure #2, 37593-4 cure #3, 37593-5 cure #2

Postcure: Time (hrs)/Temp (°F) 1/122, 1/167, 1/185, 1/203, 16/212, 1/230, 2/237

Shore A-2 readings:

Sample No.	Before P.C.	122°F		167°F		185°F		203°F		212°F		230°F		237°F	Final
		1/2 hr	1 hr	1/2 hr	1 hr	1/2 hr	1 hr	1/2 hr	1 hr	1/2 hr	1 hr	1/2 hr	1 hr	1 hr	
37593-1 cure #4	42	42	41	--	44	44	43	43	46	47	47	48	--	48	48
37593-2 cure #3	51	52	52	--	54	57	58	60	66	69	69	69	--	69	69
37593-3 cure #2	95	96	97	--	98	98	98	98	98	98	98	98	--	98	98
37593-4 cure #3	41	41	40	--	40	41	41	40	42	42	42	45	--	45	45
37593-5 cure #2	37	37	37	--	37	37	37	36	40	40	40	42	--	42	42

D. Samples No. 37593-1 cure #5, 37593-2 cure #4, 37593-1 cure #6, 37593-2 cure #5,
37593-3 cure #3, 52905-1 cure #1, 52905-2 cure #1

Postcure: Time (hrs)/Temp (°F) 16/122, 1/158, 1/176, 17/212, 1/230, 1/239, 2/257

Shore A-2 readings:

Sample No.	Before P.C.	122°F		158°F		176°F		212°F		230°F		239°F		257°F		Final
		16 hr	1/2 hr	1 hr	1/2 hr	1 hr	1/2 hr	1 hr	1/2 hr	1 hr	1/2 hr	1 hr	1/2 hr	1 hr	1 hr	
37593-1 cure #5	40	40	38	39	39	39	39	42	43	44	44	44	44	44	44	44
37593-2 cure #4	53	53	50	50	50	50	50	61	64	64	64	64	64	64	64	64
37593-1 cure #6	37	37	38	39	39	37	38	42	42	42	42	42	42	42	42	42
37593-2 cure #5	47	52	52	52	52	52	58	63	64	64	64	64	64	64	64	64
37593-3 cure #3	--	78	60	76	78	80	91	85	86	88	88	88	89	90	90	90
52905-1 cure #1	42	42	43	43	43	42	45	4	45	45	45	45	45	45	45	45
52905-2 cure #2	40	42	41	42	42	42	44	40	46	46	46	46	46	46	46	46

E. Samples No. 52911-1 cure #1, 52911-2 cure #1, 52912-1 cure #1, 52912-2 cure #1

Postcure: Time (hrs)/Temp (°F) 16/122, 1/158, 1/176, 16/212, 1/230, 1/239, 1/257

Shore A-2 readings:

Sample No.	122°F 16 hr	158°F 1 hr	176°F 1 hr	212°F 16 hr	230°F 1 hr	239°F 1 hr	257°F 2 hr	Final
52911-1 cure #1	38	40	40	44	44	44	44	44
52911-2 cure #1	33	33	33	34	35	36	36	36
52912-1 cure #1	36	37	37	42	42	42	42	42
52912-2 cure #1	32	33	33	34	34	34	34	34

After the samples were postcured, tensile specimens were cut and tested on the table model Instron. Conditions of the tensile test were: 20 inches/min chart speed, 20 inches/min crosshead speed, and 1 inch gage length between jaws. Results from this test can be found in Table 8.

APPENDIX G.

SURFACE PREPARATION OF METAL ADHERENDS

Stainless Steel

Degrease with methyl ethyl ketone, followed by a vigorous brush-scrubbing with Ajax cleaner moistened with warm water. Rinse thoroughly with tap water and inspect for a uniform water film. Oven force-dry at 180°F-200°F for 15 minutes and subject to the following etch:

841 ml - 35% hydrochloric acid

89 ml - 85% o-phosphoric acid

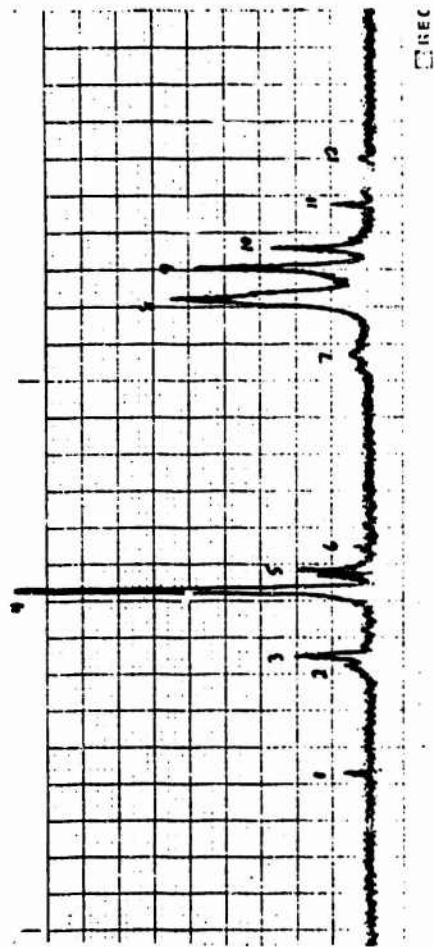
43 ml - 60% hydrofluoric acid

The acid mixture is placed in a polyethylene tray of suitable size sitting in a bubbling water bath (180°-190°F). The panels are etched for a width of one inch along the bonding edge for two minutes, then thoroughly rinsed with distilled water and oven force-dried for 15 minutes at 180°-200°F. Bonding operations should begin as soon as possible after completion of the etching operation.

APPENDIX H.

LIST OF SOLVENTS

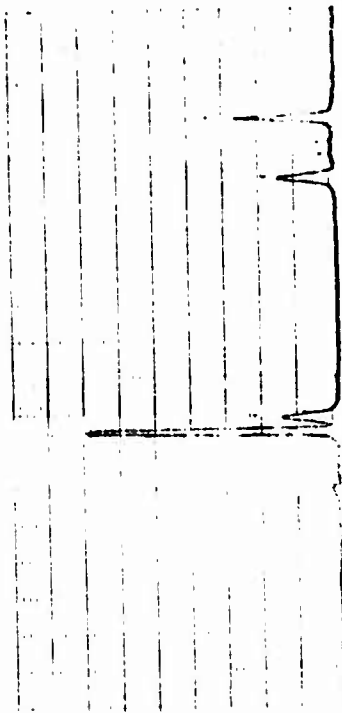
FC-75



Peak	1	2	3	4	5	6	7	8	9	10	11	12
PPM	-20.5	-5.6	-4.4	+4.8	+7.4	+10.8	+37.4	+45.0	+49.4	+52.0	+58.0	+64.5
Area Ratio												

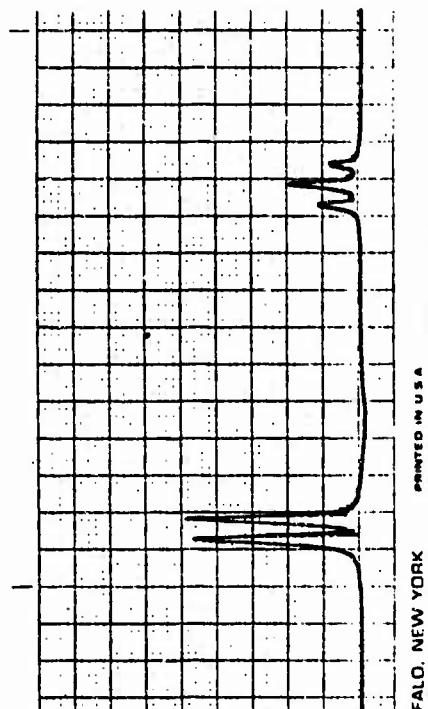
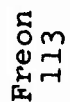
Nuclear Magnetic (F^{19}) Resonance Spectrum of Fluorochemical FC-75

FC-43



Peak	1	2	3	4	5	6	7
PPM	4.4	+4.6	+6.8	+40.2	+43.6	+45.2	+48.5
Area Ratio							

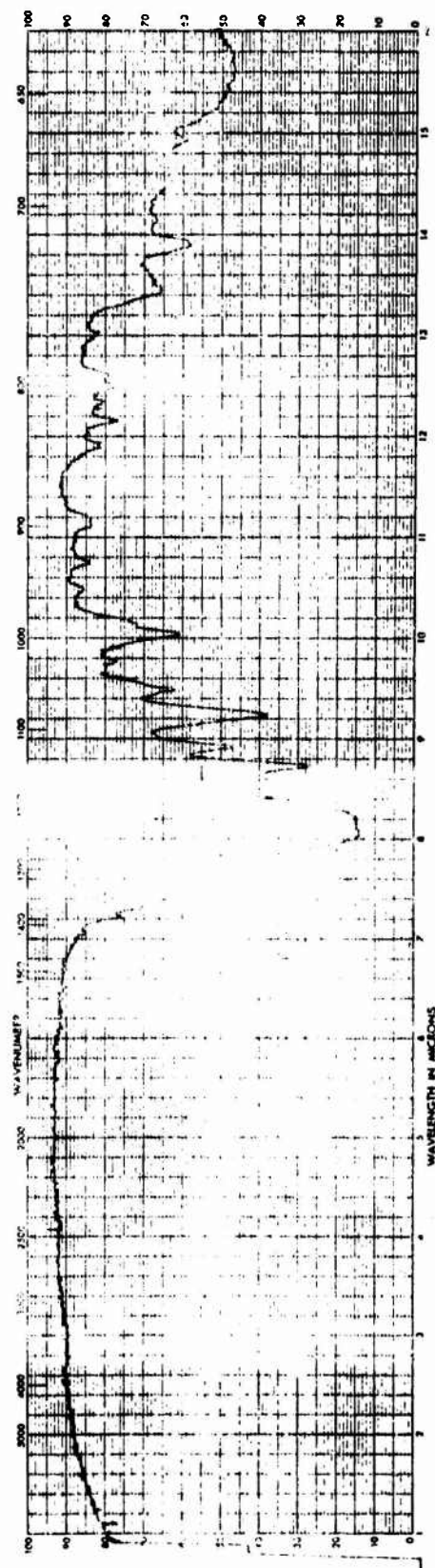
Nuclear Magnetic (F¹⁹) Resonance Spectrum of Fluorochemical FC-43



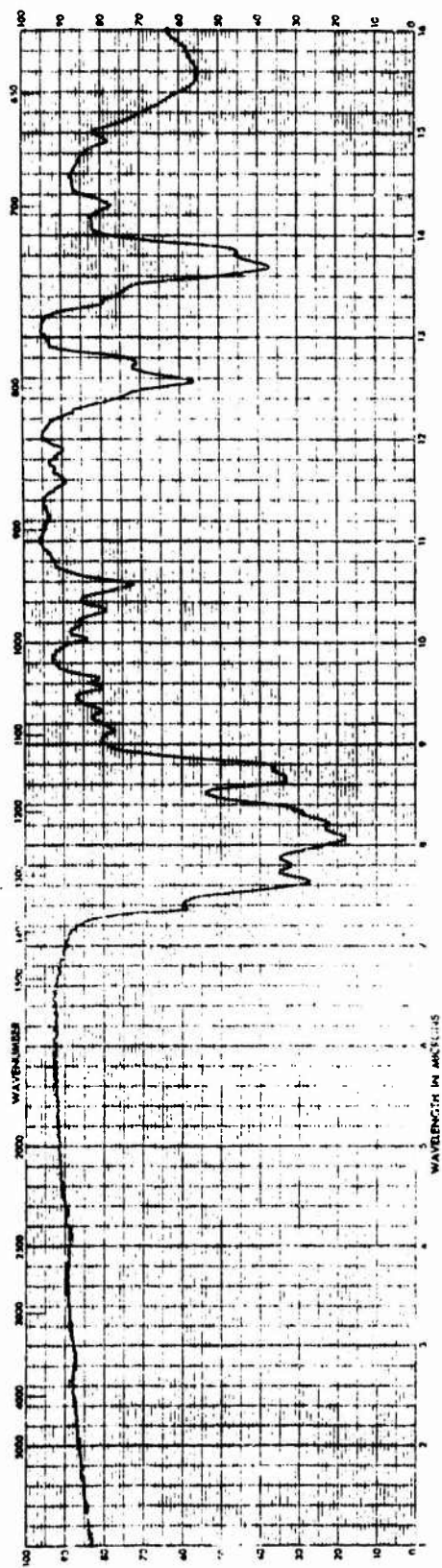
ALSO, NEW YORK
PRINTED IN U.S.A.

Peak	1	2		- Slow Sweep
PFM	-10.0	-6.0		
Area Ratio				

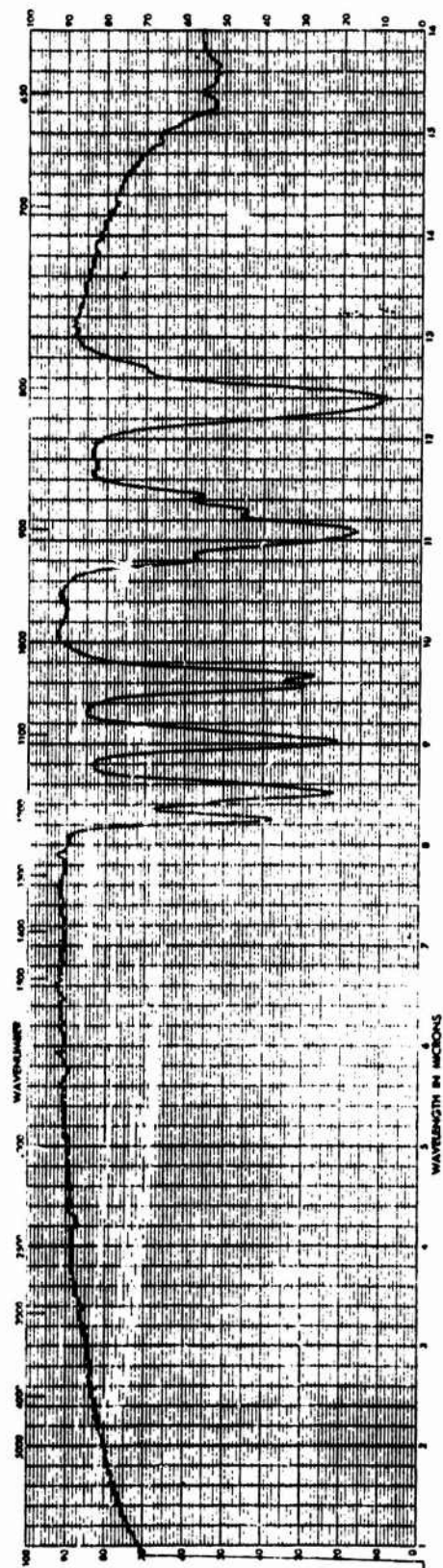
Nuclear Magnetic (F^{19}) Resonance Spectrum of Freon 113



Infrared Spectrum of Fluorochemical FC-75



Infrared Spectrum of Fluorochemical FC-43



Infrared Spectrum of Freon 113

UNCLASSIFIED

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13. ABSTRACT Characterization of the copolymer trifluoronitrosomethane/tetrafluoroethylene was completed. The gum stock was primarily produced by the Thiokol Chemical Corp. and was supplied by the U.S. Army Natick Laboratories. No sample was submitted as a representative of a production batch of the copolymer. The $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ copolymer was shown to be a low temperature rubber with probable high solvent and chemical resistance and with a reasonable thermal stability up to 250°C . As received, the $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ gum was not readily cross-linked into a high-strength rubber. The gum samples consisted of 25-50% insoluble gel and ~3% insoluble basic magnesium carbonate trihydrate. The structure was shown to be: $\text{N}-\text{CF}_2-\text{CF}_2-\text{O}$. Violent decomposition of both the $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ gum and rubber occurred at CF_3 ~ 260°C . The initial decomposition was confirmed to be: $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4 \rightarrow \text{COF}_2 + \text{CF}_3\text{N} = \text{CF}_2$. The glass transition temperature of the gums covered a range of -41° to -49°C and that of the rubber was ~ -49°C . The typical gum exhibited a bimodal molecular weight distribution with a lower portion at $\sim 2 \times 10^5$ and a higher portion at $\sim 6 \times 10^6$. A typical average M_w , M_n , and M_w/M_n was: $M_w = 3.4 \times 10^6$, $M_n = 2.7 \times 10^4$, and $M_w/M_n = 125$. The Mark Houwink equation for $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ in FC-75 at 25°C is: $[\eta] = 3.2 \times 10^{-5} M_w^{0.72}$. Optimized cure conditions showed that lower cure temperatures and longer cure times were advisable, that $M_2\text{O}$ was valuable as a scavenger filler, and that the PCR-bulk-polymerized gum provided a significantly better rubber. The best mechanical properties obtained were 387 psi tensile strength and 527% elongation. Impurities and extremely high molecular weights were detrimental to providing good mechanical properties.			

DD FORM 1473

REPLACES DD FORM 1473, 1 JAN 64, WHICH IS OBSOLETE FOR ARMY USE.

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Testing	8					
Evaluation	8					
Physical properties	8,9				9	
Rheological properties	8,9		9			
Chemical properties	8,9		9			
Rubber	9		9		9	
Nitroso Rubber	9		9		9	
Fluoronitroso rubber	9		9		9	
Measurement			8		8	
Viscosity			9			
Solvents			9,10			
Resistance			9			
Range (extremes)					9	
Temperature					6,9	
Flexibility					7,9	
Strength					9-	

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